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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 26 Portland Place, London, W.1, on 3 April 1957, the Chair being taken by The Rt. Hon. Lord Geddes, President of the Institute.

The General Secretary read the minutes of the previous meeting, which were confirmed and signed as a correct record. He also announced the names of members elected since the previous meeting.

The Chairman, introducing the author of the paper to be presented, said: This evening Mr J. L. Putman is to talk to us about some applications of radioactivity in the petroleum industry, and for this purpose has selected certain examples to illustrate the diversity of the techniques employed. These vary from the use of isotopes as tracers to the radiation of hydrocarbons and gamma-rays. Mr Putman first joined the Atomic Energy Research Establishment in 1946, in order to carry out research on Geiger counters. In 1947 he formed the Radioactive Standards Section at Harwell and since 1950 has been head of the Physics and Industrial Applications Group of the Isotope Division. He will be assisted by Dr G. P. Cook, head of the Chemistry Group of the Isotope Division.

SOME APPLICATIONS OF RADIOACTIVITY IN THE PETROLEUM INDUSTRY*

By J. L. PUTMAN †

SUMMARY

The new techniques associated with artificial radioactivity have found important uses, especially in analysis and process control, in almost every branch of industry and applied research. The petroleum industry makes greater use of these techniques, both in diversity and in numbers of applications, than any other industry.

This is not intended as a comprehensive review of the applications of radioactivity in this field—indeed an excellent review of the subject has been published recently.[1] An attempt will be made, however, to illustrate how radioactive methods are used in all phases of the industry, by means of selected examples.

DEFINITIONS

RADIOACTIVE isotopes, with which we shall be concerned, are species of the elements produced artificially, usually by exposing natural materials to the large numbers of neutrons existing inside a nuclear reactor. Chemically, they differ no more from their stable counterparts than the stable isotopes found in nature differ from one another. They are generally characterized by their atomic weight, which is the only property in which isotopes differ from one another. Thus carbon-12 and carbon-13 are both natural isotopes of carbon, but carbon-14 (or C^{14}) is a radioactive isotope.

The radioactivity consists only in the fact that the atomic nucleus is unstable, and thus liable to revert to a more stable arrangement by the emission of a charged particle or some other type of radiation. The types of radiation concerned are:

Beta particles—these are high energy electrons of nuclear origin, emitted with velocities close to that of light.

Gamma rays—these are electromagnetic radiations coming from the nucleus and have properties similar to those of X-rays.

X-rays—these are emitted by some isotopes when an electron is captured by the nucleus. X-rays are also emitted when beta particles are slowed down in passing through matter. The energy of a particle is the total energy released in bringing it to rest and is usually measured in millions of electron-volts (MeV).

DETECTION

The radiations are detected chiefly through the ionization they produce in passing through matter.

Ionization chambers—consisting of two electrodes at different potentials, are arranged to collect and record this ionization as a measure of quantity of radiation.

Geiger counters—named after their inventor, are in essence discharge tubes which are triggered off by the passage of radiation through them. They deliver a pulse of electric current for each particle or photon of radiation detected, and these electric pulses can be analysed and recorded electronically.

Scintillation counters—these rely on the production of scintillations of light when radiations are absorbed in some transparent phosphors, such as sodium iodide. A photomultiplier, used in conjunction with the phosphor, delivers electrical pulses corresponding to the flashes of light. These detectors are particularly suitable for counting gamma radiations.

* MS received 30 November 1956.

† Atomic Energy Research Establishment, Harwell.

WELL AND BOREHOLE LOGGING

The study of underground strata by sampling techniques is usually difficult and expensive. Coring is always more expensive than drilling and involves the sinking of larger diameter boreholes. Radioactive methods are already well established as a means of borehole exploration, in which the vital information is displayed on meters and recorders above the ground, connected by cables to appropriate detectors which are lowered down a borehole. The methods fall into four main categories.

Gamma-ray Logging.[2]—This is an inspection of the natural radioactivity of the strata through which a borehole passes. A gamma-ray counter, usually a Geiger–Müller type counter modified for high gamma-ray efficiency, is lowered down the borehole, and its responses are fed to a recording ratemeter on the ground surface, so that a plot of gamma-ray counting rate against depth is obtained.

Gamma-ray Scattering.[3]—In another type of instrument, a sealed radioactive source emitting gamma rays is lowered down the borehole, together with a gamma-ray counter, separated from it by a fixed distance and screened with lead or some other heavy element from direct radiations from the source. Gamma rays from the source are scattered into the detector, giving rise to a counting rate which is mainly a function of density of the surrounding strata. The source, which may, for example, be 100 millicuries or more of cæsium-137, is strong enough to make contributions from the natural radioactivity of the strata negligible by comparison with the scattered radiation. The detector can be less sensitive than for natural gamma-ray logging.

Neutron Logging.[4]—The transfer of energy from high-velocity neutrons to matter through which they pass is most efficient when the nuclei with which they collide have the same mass as the neutrons. Thus, hydrogen atoms, whose nuclei (protons) have almost the same mass, are by far the most efficient in slowing down fast neutrons to " thermal " velocities. Neutron logging, in which a source of fast neutrons, *e.g.* a capsule of polonium–beryllium mixture, is lowered down a borehole with a slow-neutron detector, such as a boron-lined counter or one filled with BF_3 gas, provides a record which is related primarily to the hydrogen content of the strata and hence is strongly influenced by its oil or water content.

Neutron-gamma Logging.—The basis of this type of inspection is the absorption of neutrons into the nuclei of atoms. This process is the same one by which radioisotopes are prepared in a nuclear reactor, though the flux of neutrons in a reactor is many orders of magnitude higher than that obtainable from portable neutron sources. Exposure of a stratum to neutrons from a portable source for a period of time renders some atoms of the stratum radioactive. A detector, registering the total gamma-ray yield, gives information about the stratum which, taken in conjunction with other borehole logs, assists in identification.[5]

A further refinement involves the use of a scintillation counter as the gamma-ray detector. This instrument has the valuable property that the amplitudes of the output pulses are proportional to the energies of radiations absorbed in the phosphor. Hence an electronic analysis of the pulse amplitudes gives more specific information about the type of radioactivity imparted by the neutrons and sometimes permits identification of the chemical element involved.

" Prompt gamma rays " are also emitted immediately on absorption of neutrons. These represent the energy released when the constituents of a nucleus rearrange themselves after the absorption of a neutron, and they too have energies characteristic of the absorbing nucleus. Hence, when a gamma-ray scintillation counter and a portable neutron source are lowered together down a borehole, electronic selection of the resulting pulse amplitudes can be used to emphasize the contribution from particular elements. The arrangement has been used successfully to distinguish between oil and brine in porous strata, even when the source and detector are inside a well lined with steel and concrete.[6] An instrument is under development for monitoring " coning " in wells where the oil is displaced by brine.

The first three types of borehole logging are already in regular use in borehole logging operations.

RADIOACTIVE TRACERS IN OIL WELLS

The possibility of detecting and identifying radioactive materials by means of the radiations they emit has led to a variety of applications in which radioisotopes are used as a label for locating and tracing fluids,[7] especially in relatively inaccessible sites. This tracer technique has been used in several ways in oil-well engineering.

Porosity of strata, leaks, and permeable zones are investigated by pumping radioactive solutions or suspensions into a well and later logging their distribution in depth.[8] The distribution of cement used in lining boreholes or sealing off unwanted zones is examined in a similar way, by adding a radioactive iridium solution or suspension to the cement slurry before injection.

Radioactive additives, particularly those labelled with bromine-82 and iodine-131, have been found suitable tracers for ground water movements.[9–11] Although their efficiency as tracers is limited to some extent by absorption, they are superior in this respect to fluorescein and other dyes. Their usefulness in tracing injection water for pressurizing oil wells has been established.[12]

ISOTOPES IN REFINERY CONTROL

Tracer Applications.—The ease of identification of a radioactive product with detectors placed outside the container makes radioactive labelling a valuable means of following the complex flow patterns in a refinery, often by measurements outside the vessels concerned.[13] A striking illustration was the use of triphenylstibine, labelled with antimony-124, to trace the flow distribution in a large vacuum distillation column.[14] It was established, entirely by measurements with Geiger counters outside the column, that the liquid in the bubble caps was filling only four of the eight compartments. The tracer tests, made whilst the plant was operating, were verified later when the column was dismantled for repair. The distribution of a radioactively-labelled constituent can be measured quantitatively, since the amount present in a given sample is proportional to the rate at which it emits radiations. This fact is used in measuring the uniformity of mixing of two blended constituents, one of which is made radioactive, and can be employed in a similar way to measure the degree of contamination of one product by another. For example, a leak between the different streams in a heat exchanger can be established, and the degree of cross-contamination measured, by introducing a radioactive tracer into the input of one stream and measuring the amount of radioactivity which appears at the output of the other.[13] Measurements of residence time in a reaction vessel and of entrainment of an unwanted constituent also lend themselves to radioactive tracer techniques.

Efficiency of separation can be checked with great sensitivity by radioactive labelling of the products to be eliminated. Where chemical processing is involved, however, care is required in selecting the chemical form of the tracer material, so that it remains firmly bound to the product which is to be traced.

Choice of Tracer.—The greatest strength of the radioactive tracer method lies in the fact that isotopes of the same element have identical, or nearly identical chemical properties.* Thus, a molecule with one of its atoms radioactive will behave in a chemical reaction exactly like an unlabelled molecule of the same substance. Ideally, all materials to be traced which may be exposed to chemical reactions should be labelled in this way, which suggests that the chief tracers for hydrocarbons are the isotopes of carbon and hydrogen. For some applications this is true, but unfortunately the only isotopes of these elements with half-lives longer than a few minutes are carbon-14 (5600 years) and hydrogen-3, or tritium (12·3 years). Both of these isotopes present some difficulties in measurement because they emit only low energy beta particles: they are therefore not easy to use for measurements on a plant scale except by sampling techniques. Carbon-14 and tritium labelling of the molecules themselves do provide powerful tools for the research chemist, however, and the mechanisms of certain reactions have been investigated on a large scale with their aid. Probably the best-known examples are the investigations[16] into the Fischer–Tropsch synthesis of hydrocarbons, using carbon-14-labelled catalyst and feed materials.

In many important applications, however, where only the physical movement of components is to be traced, one can choose isotopes of other elements whose chemical properties are such that they remain firmly bound to the material to be traced, but whose radiations are especially suitable for the measurements to be done. The flow rate and the degeneration of catalyst particles in a cat-cracker have been measured using antimony-124, barium-140, and other gamma emitters firmly adsorbed to the catalyst surfaces.[17] By the choice of tracers emitting gamma-rays of different energies, several samples of different catalyst materials have been tested simultaneously in a cat-cracker to compare their performance.[18] A scintillation counter was used as detector and, by electronically selecting the pulse amplitudes, as described above, the three tracers cerium-144, chromium-51, and scandium-46 could be distinguished.[19]

The above are only a few of the many ways in which radioactive tracers are used in the refinery. For fuller accounts the reader is referred to reviews of such work.[1, 13-14]

Level Gauges and Thickness Gauges.—The absorption of radiations in passing through matter is used in some equipment which embodies a sealed radioactive source and detector placed on opposite sides of an object to be tested. In a simple application, the level of liquid in an enclosed vessel can be monitored by placing the source and detector at the same level, the source being chosen so that its radiations can penetrate the walls of the container to the detector when the liquid level is low, but are heavily absorbed by the liquid when the level is high.

More refined measurements of the absorption of radiations can be used in density measurements of fuels, to be described later.

The scattering back of gamma rays which fall on the wall of a pipe or a tank is used as a measurement of thickness of the tube walls from the outside. This is the basis of a portable instrument[20] which has now

* There are indeed some small differences in rates of reaction (isotope effect), between different isotopes of the lighter elements,[15] but these are rarely very significant except in recycling chemical processes. Even these effects are due to mass differences only, and there is no more difference between radioisotopes than between stable isotopes of a natural element.

been in routine use in a refinery for the last three years in checking pipes for internal corrosion.

ANALYSIS OF PRODUCTS

Estimation of Sulphur and Lead.—The absorption of X-rays by hydrocarbons is very much less efficient than by elements of higher atomic number. Thus, when X-rays of suitable wavelengths pass through a cell containing a refined hydrocarbon product, small contaminations of sulphur-containing compounds play a major part in determining the number of radiations which emerge.

Gauges employing X-ray tubes as sources of X-rays between 0·5 and 5 Å in wavelength have been used for some time for the continuous estimation of sulphur in refined fuels.[21] Sensitivity of the order of 0·05 per cent by weight is available. Tetraethyl lead can be estimated in a similar way with even greater sensitivity.[22]

An improvement in stability of X-ray intensity, as well as a simplification of the apparatus, is achieved by replacing the X-ray tube with a radioactive source of X-rays. The electron capture isotope Fe^{55}, with a half-life of 2·9 years, emits X-rays of wavelength about 2·1 Å and has been used successfully for this purpose.[23]

A very recent development makes use of the secondary radiation (*bremsstrahlung*), which is emitted when beta particles are absorbed in a medium.[24] Tritium, an isotope of hydrogen, with a half-life of 12·3 years, gives rise to *bremsstrahlung* with a mean wavelength of about 2 Å and has been found a suitable source for sulphur determinations by X-ray absorption. Similar sensitivity is obtainable, but the relative cheapness of tritium and its long radioactive half-life makes this method cheap and practical for routine determinations.

Carbon–Hydrogen Ratio.—The absorption of beta particles and gamma rays in passing through matter is mainly due to energy losses to the atomic electrons. The degree of absorption is thus a direct measure of the number of electrons encountered, and since for the light elements the atomic weight is nearly proportional to the atomic number ($Z = 6$, $A = 12$ for carbon), the absorption coefficient is nearly proportional to density. Hydrogen, however, is an exception, having one electron ($Z = 1$) and an atomic weight of unity ($A = 1$). Thus hydrogen is twice as efficient as carbon, mass for mass, in absorbing beta and gamma radiations.

By simultaneous measurement of the density of a fuel, and of the reduction of a beam of beta or gamma radiations in passing through a fixed thickness of it, the proportion of hydrogen can be determined quickly and accurately.[25]

An alternative method of determining hydrogen content by the scattering of neutrons from a portable neutron source has been demonstrated in principle,[26] but is not yet in general use.

RADIOACTIVATION ANALYSIS

Hydrocarbons are not made radioactive to an appreciable extent by irradiation in a nuclear reactor, though they do suffer considerable chemical degradation. Some common impurities, however, do become strongly radioactive on irradiation, and their concentration can be determined with great sensitivity in small samples.[27]

Sodium chloride, in particular, forms sodium-24 and chlorine-38, amongst other isotopes, on neutron irradiation, and can be determined in concentrations down to 0·001 parts per million or lower by means of its radioactivity.

PIPELINE OPERATION

Interface Labelling in Batch Pumping.—In delivering refined products to storage depots through long-distance pipelines, a single pipeline must, for economic reasons, serve for the pumping of many dissimilar products. Batch pumping, in which different products follow one another along the same line, demands accurate synchronization at the output end, or large volumes of fuel may be pumped into the wrong storage tanks or down-graded through intermixing of the products. Hydrometer measurements, or other tests of the output fuel, must be both accurate and rapid if switching is to be done promptly. Timing, coupled with controlled pumping rates, helps in estimating the time of arrival, but "packing," in a line which has been out of service, can lead to errors as great as half an hour in time of arrival of the interface after a 15- or 16-hour run.

Radioactive tracers are now injected in soluble form at the interface between two products. The interface can then be detected as it passes any point by means of portable counters placed against the pipe. This indication is used to give warning of the approach of a change in product at the output end and then to give evidence of its arrival. The inevitable intermixing which occurs across the interface is measured also by the distribution of the radioactivity. It can be shown theoretically, and has been verified experimentally, that the counting rate distribution curve, recorded on a suitable scale, is the differential of the concentration curve for the following product. Thus the same method can be used to give accurate data on cross-contamination, reducing the quantity of down-graded product to a minimum. The method is used extensively in the U.S.A., with antimony-124, barium-140, or cobalt-60 as the tracer materials.[28-9] It is also used to some extent in the U.K. and bromine-82 and scandium-46 have proved to be suitable tracers.

Disadvantages of the method of radioactive labelling lie in the need for supplies of radioactive material and for suitable injection apparatus at the input to the pipeline. The small quantity of radioactive fuel is usually of little embarrassment and can be stored till the radioactivity decays away. A very promising alternative method, which relies only on rapid and accurate measurement of density near the output, has been field tested. This is achieved by measuring the absorption of gamma rays from a sealed radioactive source as they pass through the pipe to a detector on the opposite side. Using a moderately strong (300 millicuries) source of cæsium-137 as the gamma-ray source, and a standard type of ionization chamber as detector, differences in fuel densities as low as 0·1 per cent can be detected.[30] It is evident that the effective density, measured in this way, also depends on hydrogen content, but the method is still an efficient means of differentiating between successive products.

Leak Testing.—Radioactive solutions are also used to detect leaks in buried pipelines. In a recently developed method,[31-2] water containing a dilute solution of sodium-24 (as bicarbonate) is pumped along the suspect line under pressure. At leaking points, some of the radioactive solution passes into the surrounding soil. The radioactive solution is then followed by pure water to flush the inside of the pipeline.

At a suitable distance behind the radioactive "plug," a self-contained, battery-operated detector is inserted and this is towed along behind a "pig" operated by hydraulic pressure. The detector contains Geiger counters, and a miniature wire recorder, into which the output pulses of the Geiger counters are fed. A wire record is thus obtained of the distribution of radioactivity along the length of the pipeline: in particular, the activity of the soil at leaky points is recorded, together with that of small cobalt-60 wires placed at intervals along the pipe to serve as distance markers.

The wire recorder is removed at the end of a length of pipeline and is played back to an electronic ratemeter and pen recorder. A tracing is produced, which accurately indicates the positions of any leaks. At present this method has been used successfully in lines up to 20 miles long. It is hoped later to extend its use to lengths of 50 or 100 miles.

Lost Pigs.—"Pigs" or "go-devils" used as scrapers to clean out pipelines often become stuck, and although their approximate position might be known, the accurate location of a pig in a buried pipeline was a difficult and costly business until radioactive marking was used. In its simplest form, the radioactive marker consists of a sealed cobalt-60 source attached to the central shaft of the pig. The gamma rays from this source can be detected above the ground if the pipeline is not too deeply buried.[33] Depths of detection vary with the soil density, but a 100-millicurie source can generally be detected down to 3 feet below the surface if a scintillation counter is used as detector.

Even at this level of activity, the exposed radioactive source needs careful handling, and digging operations to remove the pig must be conducted in such a way as to avoid over-exposure of personnel to the radiations. In a modification[34] which largely overcomes this difficulty, the source is mounted in a lead container from which it is only ejected when under hydraulic pressure. Thus, for attachment to the pig and after detection, the source is heavily screened, but it is exposed for detection through the soil when pressure is applied to the pipeline. This modification permits the safe use of sources of 500 millicuries or more, which can generally be detected at depths down to 4 feet.

LUBRICANTS AND WEAR TESTING

Engine Wear.—An important contribution of radioactive techniques to the testing of consumer products is in the use of tracer methods for measuring engine wear. When components of an engine, such as piston rings or bearings, are made radioactive by irradiation in a reactor, wear debris from the radioactive components can be detected and measured in circulated lubricating oil.[35-8] By measuring the build-up of radioactivity in the oil, a continuous quantitative record is obtained of the wear of a particular component under running conditions.

Variations in wear rate with conditions of speed and loading can be studied without dismantling or disturbing the alignment of the engine, and in particular the wear-reducing properties of different lubricants and additives can be compared under identical conditions. Wear tests are even conducted in this way on cars whilst they are being driven.

Unfortunately iron is an element which does not acquire a high level of radioactivity on neutron irradiation, but even so, the wear of steel piston rings can be measured after a running time of $\frac{1}{2}$–1 hour, as compared with hundreds of hours when more orthodox methods of measurement are used.

As a direct result of the study of lubricant properties by these means, new and improved lubricating oils have been produced which, it is claimed, can reduce engine wear by a large factor as compared with earlier lubricants.

Wear of Machine Tools.—Similar tests are made to measure the wear of tungsten carbide cutting tools under various conditions of use and lubrication.[39-41] Tungsten is a particularly favourable element for activation by reactor irradiation: only the tool tip is made radioactive and sub-microgram quantities of wear debris can readily be measured. An advantage in this application is the ability to determine wear at various phases in the tool life.

EFFECTS OF LARGE DOSES OF RADIATION

With the introduction of atomic power, increasingly large supplies of radioactive sources will become available as fission products extracted from the treated fuel elements. This will make it possible to use sources of activity from 10,000 curies upwards in single installations for the irradiation of products. It should be noted that these sources are stronger by many orders of magnitude than the ones used in the applications so far described, which generally range from a few millicuries to 1 curie at the most.

Practical applications of high doses of radiation in modifying the properties of petroleum and its products are at present mostly conjectural, but the possibilities are interesting enough to have stimulated research by the petroleum industry in this field. Gamma rays from the fission products offer the best possibilities, because they are highly penetrating and can be used to treat material in bulk.

On absorption in a molecular structure, gamma rays release energy along their paths in quantities large enough to break chemical bonds. Thereafter their effects on hydrocarbons fall into two main categories.

In the first, heavy molecules are degraded to form lighter ones and in particular the cracking of hydrocarbons proceeds at lower temperatures.[42] There is some evidence also that the cracking pattern may be modified by the influence of high doses of radiation, and this may result in the more efficient production of high octane fuels.

Secondly, the disrupted molecular fragments may react to form larger molecules. Chemical reactions, such as the chlorination of benzene and other aromatic hydrocarbons,[43-4] have been catalysed on a laboratory scale by gamma radiation alone, and it is to be expected that some of these processes will have economic advantages.

Polymerization of monomers and the cross-linking of fractured chains in polymers have also been produced by gamma irradiation. Ethylene has been polymerized on a laboratory scale,[44-5] and cross-linking in irradiated polythene has been shown to modify it [46-7] by raising the melting-point, increasing the mechanical hardness, and introducing new elastic properties.

The general effect of irradiating lubricating oils is to increase their viscosity and to modify its temperature dependence. This is also thought to be due to some polymerization and branching of the molecular structure. Polymer additives, such as long-chain methacrylates with improved temperature stabilities, have been successfully produced by gamma irradiation,[48] but the work is still at an early stage.

CONCLUSION

The above is an incomplete and inevitably sketchy account of the great variety of ways in which the petroleum industry is using the new radioactive techniques. It is symbolic of the supporting, rather than competitive, role which atomic energy is beginning to play in our economy, that even now its by-products are serving vitally in every phase of the petroleum industry.

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Mr Putman and Dr Cook have given a number of examples of the first aspect; there is the method of detecting very small quantities of certain substances such as sodium chloride, which can be detected at concentrations of one part per thousand million; it is also possible to observe what is occurring inside a closed vessel without the necessity of entering it (the measurement of the wall thickness and the observation of partly blocked trays in a fractionating column).

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At this point, I would like to express my interest in the use of portable neutron sources, especially their use in estimating the moisture content of the soil. It is believed that in certain types of low-cost road making it is necessary to know the moisture content of the underlying surface. Could the author say whether the size and type of equipment necessary would permit its use for this particular purpose?

To turn to the other way in which the use of radioactive techniques benefits research, *i.e.* by speeding up work using existing techniques, I would like to give some further examples taken from work concerned with the measurement of wear of piston rings. For a number of years we have used engines fitted with radioactive rings for this purpose with great success. As an example of how work can be speeded up, a recent experiment should be mentioned in which we studied the effect on piston ring wear of six fuels, two lubricants, and three running conditions in every combination, each combination being repeated. This required 72 runs. To carry out this experiment with conventional methods would have taken about nine months with shift working and would have required a running time of 2500 to 3000 hours. In fact, the experiment would have been impossible, since to maintain engine condition it would have been necessary to renew rings and liners every 400 hours. Such an operation would increase the random error of the determination many times and would almost certainly have led to bias in the results. However, the total engine running time was 300 hours and the experiment took about three months to complete without shift working.

Because of the success of this method of measuring wear we are extending our facilities for using it. To avoid having separate instrumentation for every engine, a transportable apparatus which can be moved from engine to engine is being made by a well-known instrument manufacturer. This will consist of a pumping unit, scintillation counter, ratemeter, and recorder mounted on a trolley which can be moved from engine to engine. This unit will probably be available commercially.

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It was of interest to see in the paper that wear tests are conducted in this way on cars whilst they are actually being driven. I would like to ask the author whether he means that a continuous record is in this case being made in the car itself and, if so, whether he has any observations to make on the equipment necessary. At Thornton considerable progress has been made in the design of such equipment, the aim being to make as little demand on the power supply of the car as possible. A very compact high-tension transistorized power supply and a special recorder, both worked directly from the car battery, have already been successfully completed, and we are now

EFFECTS OF LARGE DOSES OF RADIATION

With the introduction of atomic power, increasingly large supplies of radioactive sources will become available as fission products extracted from the treated fuel elements. This will make it possible to use sources of activity from 10,000 curies upwards in single installations for the irradiation of products. It should be noted that these sources are stronger by many orders of magnitude than the ones used in the applications so far described, which generally range from a few millicuries to 1 curie at the most.

Practical applications of high doses of radiation in modifying the properties of petroleum and its products are at present mostly conjectural, but the possibilities are interesting enough to have stimulated research by the petroleum industry in this field. Gamma rays from the fission products offer the best possibilities, because they are highly penetrating and can be used to treat material in bulk.

On absorption in a molecular structure, gamma rays release energy along their paths in quantities large enough to break chemical bonds. Thereafter their effects on hydrocarbons fall into two main categories.

In the first, heavy molecules are degraded to form lighter ones and in particular the cracking of hydrocarbons proceeds at lower temperatures.[42] There is some evidence also that the cracking pattern may be modified by the influence of high doses of radiation, and this may result in the more efficient production of high octane fuels.

Secondly, the disrupted molecular fragments may react to form larger molecules. Chemical reactions, such as the chlorination of benzene and other aromatic hydrocarbons,[43-4] have been catalysed on a laboratory scale by gamma radiation alone, and it is to be expected that some of these processes will have economic advantages.

Polymerization of monomers and the cross-linking of fractured chains in polymers have also been produced by gamma irradiation. Ethylene has been polymerized on a laboratory scale,[44-5] and cross-linking in irradiated polythene has been shown to modify it [46-7] by raising the melting-point, increasing the mechanical hardness, and introducing new elastic properties.

The general effect of irradiating lubricating oils is to increase their viscosity and to modify its temperature dependence. This is also thought to be due to some polymerization and branching of the molecular structure. Polymer additives, such as long-chain methacrylates with improved temperature stabilities, have been successfully produced by gamma irradiation,[48] but the work is still at an early stage.

CONCLUSION

The above is an incomplete and inevitably sketchy account of the great variety of ways in which the new radioactive techniques. It is symbolic of the supporting, rather than competitive, role which atomic energy is beginning to play in our economy, that even now its by-products are serving vitally in every phase of the petroleum industry.

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coping with the design of a pumping unit which will be able to pump oil from the sump to the count up to the highest viscosities likely to be met in practice.

There is one type of engine in which we are anxious to devise some means of obtaining data on wear more rapidly than by conventional techniques, but to which a radioactive technique does not at first sight seem applicable. This is the large marine diesel, which has a total loss cylinder lubricating system. In these engines, the wear débris is ejected with the lubricant through the engine exhaust. The method of measuring the activity of the crankcase oil, which is used for trunk engines, is obviously quite inapplicable. Has Mr Putman any suggestions to make in this direction?

Another way in which radioactivity has speeded up engine research is in the measurement of the build-up of engine deposits by the insertion of a radioactive plug into the cylinder head of the test engine.

The use of radioactivity has its limitations and drawbacks. The first and most obvious is the health hazard, and it is absolutely imperative that no risks are taken. Another limitation, certainly applying to work on wear, is that the engine parts involved become inaccessible to visual observation. There is much more to the study of wear than the determination of how much metal is rubbed off a component—one also wants to know from which part it was removed and how it was removed. It seems as if conventional methods will still have to be relied upon. Another factor which has to be watched is that wear tests which are carried out very rapidly may show different trends from those which are carried out over longer periods. There is also a popular misconception which confuses sensitivity with precision. With radioactive techniques one can measure accurately very small amounts of material of a certain kind in the system. However, if the process which produces this change is subject to random or controlled fluctuations, then the overall precision of the measurement may not be of a high order. Something of this kind seems to occur in engine wear tests, for the precision of wear measurements in the tracer engine is not much better than that in the normal engine. This is presumably because the wear process itself is irregular. Hence, even with this advanced technique one must still plan experiments carefully to avoid bias.

Finally, I should like to remark that the great assistance which the atomic energy industry is rendering to the petroleum industry is not entirely one-sided. New types of nuclear reactor will require lubrication, and the lubricants will have to withstand very severe and unprecedented conditions. Some of the effects which such conditions could have are indicated in the last section of Mr Putman's paper. The petroleum industry is working hard and, I believe, with considerable success, to meet the demands imposed on it by the operation of these reactors.

The release of nuclear energy has not been an unmixed blessing, and all of us must often be worried about some of its effects on the future of the human race. However, if one concentrates on the credit side, it seems likely that in the long run the direct benefit which the world obtains from nuclear energy in the solution of the problem of energy resources may be surpassed by the indirect benefit resulting from applications such as are outlined in the paper, since these could apply to all aspects of material life.

J. L. Putman: The contributions of Thornton Research Centre to wear measurements have certainly been very great, and I have enjoyed hearing Mr Epton's account of this work, some of which is quite new to me. I must apologize if, in all good faith, I have exaggerated the saving of time in using isotope methods for testing the wear of engines. It would appear that orthodox measurements of wear estimation have improved on the figures to which I had access, if the average running time for a single test is only 35 to 40 hours. However, Mr Epton has demonstrated a saving of running time by a factor of 10 in testing piston rings, and I suggest that the factor might be considerably higher when heavier components are involved. Moreover, I believe Thornton Research Centre did demonstrate a test engine in which wear rate could be estimated by radioactive measurements in half an hour, but perhaps not with the required precision.

Enlarging on this question of precision, I fully agree that it should be distinguished from ultimate sensitivity. As a general rule, radioactive counting methods cannot be expected to yield results much more accurate than $\pm 1\%$ of the quantity measured. This is a matter of stability of detectors and associated electronic circuits, as well as the statistical nature of the radiations themselves. Under some conditions better stability can be obtained, but for general research purposes 1% accuracy is about the best which can be expected. Moreover, when results rely on small differences of large quantities, accuracy may be much worse, and experiments should be designed if possible to avoid this source of error.

I should like to emphasize, however, that fluctuations in results which are attributable to real fluctuations in wear rate do not invalidate the accuracy of this more sensitive method of measurement. In so far as these fluctuations limit the speed of measurement by radioactive means, they would seem to set an ultimate limit to the speed of any method of test. Similar fluctuations have been found in radioactive measurements of the wear of wire-drawing dies, and these also appear to correspond to real irregularities in wear rate. I believe Thornton Research Centre has shown, by short-period radioactive measurements, how wear rate changes with ageing of the machine and of the lubricant (a demonstration which is impossible when long running is necessary for each measurement). May it not be that the interpretation of these still shorter term fluctuations could throw light on the nature and mechanism of the wear processes?

An autoradiographic examination of wear débris on wires passed through a radioactive drawing die threw interesting light on the nature of wear from the die. The wire-drawing die consisted of tungsten carbide in a cobalt matrix, and after irradiation contained both radioactive W^{185} (half-life 74 days) and Co^{60} (half-life 5·23 years). Wear débris could thus be identified by the comparison of intensities in autoradiographs taken at intervals. It was found that although cobalt was worn off smoothly and fairly uniformly, tungsten was removed in relatively large discrete particles. Perhaps the method is not directly applicable to the study of machine wear, but an autoradiograph of a sample of débris settled from the lubricating oil might throw valuable light on particle size.

The difficulty of visual observation during radioactive wear tests is not necessarily insuperable on account of the health hazard. It is true that large components under test must carry high levels of radioactivity (generally some hundreds of millicuries) if they are uniformly labelled with radioactivity such that very small amounts of wear débris are measurable. It is true also that radioactive labelling of surfaces, although it saves in total activity in the engine, is rarely satisfactory except for

plated components, because of the difficulty of reproducing the working surface. However, if inspection panels can be fitted in such a way that they neither upset the working of the engine nor become fouled with lubricating oil, they could be viewed through a lead glass window in a lead screen (2 inches of lead glass is roughly equivalent in protection to 1 inch of lead) or by mirror systems around such a screen. May I respectfully suggest that stroboscopic inspection under these conditions might provide further information as to the nature of the wear?

To the best of my knowledge, radioactive wear tests have in fact been made on cars whilst they were being driven. However, I believe these experiments have not yet been published, and I regret I am not in a position to comment on the equipment used.

I know of no way to extend these methods to large marine-type engines. If a representative sample of the débris could be collected at the exhaust, an estimate of its specific activity might show what proportion of the total wear originated from a labelled component. I doubt if this could give a very accurate measure of component wear, and certainly it would not compare in speed with the results obtainable with circulating lubricants.

The neutron scattering method can be adapted to the determination of moisture for rapid road construction, and a very portable unit for this purpose is being developed at A.E.R.E.

May I say how the services of the petroleum industry to the atomic energy effort are appreciated and relied upon by our friends the power engineers, even though we of the Isotope Division enjoy them only indirectly as yet.

Lord Geddes: There has been no mention of cost. One gets the impression, more particularly from the power side, of fantastic figures the moment one hears of Harwell. There was a debate in another place when quite astronomical figures were being discussed in relation to the costs which are being incurred in nuclear power development. These may be only the luxuries of Mr Putman's friends in the Power Division, but it would be interesting to have some information as to whether these applications of radioactivity that he has been telling us about are very expensive or are within a reasonable range of the expense that one would otherwise incur.

J. L. Putman: I am fairly sure that if the figures were astronomical they probably referred to the nuclear power industry. The cost of the radioactive materials themselves, as supplied from Harwell, is almost negligible in comparison with the amount of work one can get out of them. We estimate that the saving of money in time, material, and improved quality control by the use of isotopes in the U.K. alone, is probably more than £10 million a year. On the other hand, the turnover from the direct sale of radioactive materials from Harwell is of the order of a million pounds a year or less. This includes our exports to the whole world, and we do export to most of the Western world. The cost of the material to the individual is often the cost of a single irradiation unit, which is a measure of quantity of material in terms of the neutrons it absorbs in a reactor. A single irradiation unit, irradiated for one week in the reactor, costs £3; the charge for one month is £6. The greater cost is in the detectors. The most generally used type of detector is the Geiger counter, and different designs of these are used for beta-particles and gamma-rays. The usual price of these is from £3 to £5. The electronics associated with them are more expensive. Portable equipments vary from about £30 to about £200, and, for laboratory use, a scaler and a power unit can be obtained for about £200. Thus, for research purposes, a small tracer research laboratory can be set up at a cost of about £500.

G. E. T. Eyston: Mr Putman touched on the question of analysis of lubricating oils. Could he tell us, without going into detail, whether it would be at all practical to assume that there might be a possibility of detecting a loss of active metal compounds in a lubricating oil when running an engine under varying conditions? It would be very interesting to determine the rate of loss of additive compounds.

J. L. Putman: It is always difficult to measure a rate of loss by radioactive means, because one is trying to measure small differences of large numbers. If the loss is, in fact, a physical loss and not a chemical degradation, and if there is any means of knowing where the additives are going, then supposing that they can be labelled radioactively, they can be picked up in that other location with much greater accuracy. This would not in fact be a direct measurement of loss, but rather a measurement of the fate of these materials.

The possibility of labelling depends on the elements present in the additive. Most of the metals in fact can be made radioactive to a fairly high level of activity, though the type of radiation and the radioactive half-life are different for different metals, and some of the radioisotopes formed are too short lived for convenience.

The question of health hazard was raised earlier, and it is worth pointing out that in many tracer experiments the health hazard arises because one is trying to measure, in wear for example, a very small proportion of a relatively large amount of radioactive material.

Sometimes one can get around this problem, if the constituent which is to be detected is of a different nature from the base material. To quote an application from the glass industry, it was required recently to determine the fate of selenium, which is added to glass as a de-colorizer during its manufacture. Tracer measurements were to be made on a production scale, using 200 tons of glass. It would have been necessary, using ordinary tracer techniques, to add enough radioactive selenium to label the whole of this 200 tons. Instead of this, samples of glass were taken, one of which contained no selenium additive, the other containing the amount of selenium to be determined. By irradiating these side by side in a reactor and comparing the radiations which were emitted by them, a response was obtained which corresponded to the amount of selenium present. This was done without introducing any activity into the factory at all.

R. H. W. Hamilton: I would like to ask Mr Putman, particularly in relation to safety, whether he thinks it would be a reasonable thing to carry out the proposal, made in the paper, for using these modern methods to determine the whereabouts of cement down a borehole. This has always been done by the measurement of temperature change occurring in the cement while it is hardening. That is not in practice a very good arrangement, for the curves tend to flatten out at the very point where they should be peaks, and this new method seems to open up a great possibility. I would be very interested to know whether he feels that the new technique could be carried out safely from the operator's point of view, or whether our workpeople might be affected as a result of the operation.

J. L. Putman: I regret having no personal experience of this technique, but it is in routine use by at least one oil drilling company in the U.S.A. and also in Trinidad. American regulations concerning the use of artificial radioactivity are very stringent, so this indicates that the method is safe when applied with reasonable precautions.

Once the radioactive material is in the borehole and more than two or three feet below the ground surface, no appreciable amount of gamma-radiation can penetrate to the surface. The only possible hazards arise from the handling of the cement slurry before injection.

There are two possible dangers from any radioactive material. One concerns the exposure of the body to radiations from an outside source. This must be kept within prescribed limits, which can be satisfied by adequate screening precautions and operation from a suitable distance. Not more than from 1 to 5 millicuries of activity per ton of slurry is likely to be necessary, and this level of activity is not difficult to handle safely, especially as most of the gamma-rays arising from a large bulk of material are absorbed inside it before they reach the surface.

The second possible hazard arises from ingestion of the radioactive material, in this application as dust by breathing or as dirt accidentally wiped across the mouth. The dust hazard can be kept negligible when dealing with a wet slurry, and passage of dirt through the mouth is avoided by handling the material only with tools and under controlled conditions.

In short, there seems no reason, from health considerations, why this method should not be generally adopted.

Dr M. F. Hoare: Mr Putman has given an extremely comprehensive review of the type of problem which is being solved in the oil industry by the use of tracer techniques. In his presentation, however, he did not deal with the question of radiation chemistry.

The published data on radiation effects in hydrocarbons are somewhat limited, although a considerable amount of work is going on in this field. Perhaps the greatest publicity has been given to the radiation treatment of polymers, in particular polythene. Graft polymerizations of monomers on to preformed polymers have been studied extensively by the French school under Magat. Other work in the U.S.A. has been concerned with catalysis of chlorination reactions. These examples serve, however, to illustrate one important point to be constantly borne in mind when assessing the potentialities of radiation as a reaction promoter. This is that the actual number of molecules which are affected by radiation is relatively small, and only if these activated molecules set off reactions of long chain length, such as in graft polymerization, or are of very high molecular weight, such that the reaction of very few molecules serves to alter physical properties, as in the case of irradiation of plastics, is the use of radiation likely to prove economically favourable for production of large volume products.

Some references have been made to the use of radiation in assisting oil cracking. Data have been published in the U.S.A. by Atlantic Refining on the irradiation of materials such as dodecane, whereby higher molecular weight materials were obtained after a very high radiation dose. These experiments were carried out at fairly low temperatures. Chain lengths for these types of reaction are very small and if one wishes to obtain oil cracking reactions under conditions where chain lengths are reasonable one has to go to higher temperatures. Under these conditions there is a competition between thermal and radiation initiation.

I would like to be a little more specific on this point in order that many of the rather vague statements on the effect of radiation on oil cracking, etc., may be put into a truer perspective. In the radiation attack on a hydrocarbon it may be said that about 3 molecules are decomposed for every 100 electron volts of energy deposited. Relating this to a dose rate it means that one roentgen of radiation will cause the initial breakdown of about 2·5 times 10^{-8} per cent of a hydrocarbon of molecular weight 100. This breakdown will be directly proportional to the molecular weight and to the chain length of the reaction. If we consider a cobalt 60 source with a maximum practical dose rate of 10^6 roentgen per hour, this means that a hydrocarbon can be decomposed at the rate of 0·02 per cent per hour if initial decomposition is the only effective reaction. This rate of decomposition is several orders of magnitude lower than that for normal thermal and catalytic processes encountered in a refinery and, unless subsequent reactions are of an adequate chain length, of the order of 50 to 100, mere throughput limitations will put this type of radiation initiation out of court. Combination of radiation and thermal initiation for a reaction may provide a solution for obtaining a sufficiently high conversion by inducing longer chains, but in this case any marked effect of radiation will only be present at very high dose rates. In hydrocarbon cracking, chain lengths have been quoted by Hinshelwood and others of the order of 10, and hence one would need radiation doses of at least 10^7 roentgen per hour to give a rate of initiation by radiation which is comparable to that of the thermal initiation. The possible use of strontium sources to obtain such dose rates cannot be neglected, and I would like to ask Mr Putman his views on this last point.

J. L. Putman: I am indebted to Dr Hoare for his lucid expansion of the possibilities and limitations of radiation chemistry. In reply to his question about the use of strontium-90 to obtain high dose rates, I think that this is a very promising idea. The limited range of strontium beta-particles does rather restrict the use of this isotope to operations through small thicknesses of liquid or gaseous media, and to processes in which the radioactive source itself does not become gummed up by solid products, which can prevent the further escape of radiations. Provided processes of the kind he was describing can be conducted in liquid media, then I think that the flowing of liquid products, for example, through beds of glass beads impregnated with strontium-90 might be a very promising method of application, provided that means exist for concentrating the strontium-90 isotope into small volume. I believe that the possibilities of re-concentrating strontium into glass beads, or into other possible materials are still being explored. The requirement is for a medium which can be packed into a bed, to do its work locally, and yet to have radioactivity distributed over a large body through which the material to be treated will pass. The concentration of strontium in this way very largely depends on the specific activity which is obtainable, and the specific activity obtainable in strontium-90 produced from fission products is limited. The specific activity of fission-product strontium is not likely to be increased appreciably as the power and the neutron flux of new reactors goes up. However, as the flux of power reactors is increased, and as the number of reactors is increased, vast quantities of strontium-90 and of cæsium-137, the two main fission products, will become available. If some really economic

way of using strontium-90 could be found, it would certainly pay high dividends.

Dr E. J. Gibson: There are two points arising from Mr Putman's paper. The first is concerned with the accuracy which he can get using cæsium-137 as a gamma-ray source to determine the density differences between oils flowing in a pipe; he claims that density differences of 0·1 per cent can be determined. At the Fuel Research Station we have been using cæsium-137 for some time as a gamma-ray source to measure the level of liquid inside a pressure reactor with gas bubbling upward through the liquid, and the accuracy of density changes which we can detect there are of a different order. We are using about 20 millicuries cæsium only, and detecting not with an ionization chamber, but with a Geiger counter. The limits of our accuracy are determined by the accuracy of the electronic instrument, the ratemeter, and it is down to something of the order of 1 to 1½ per cent. I would be glad if he would suggest some means whereby we could increase the accuracy of our readings.

The second point is the use of soft X-rays. The use of soft X-ray absorption to measure the sulphur content of petroleum oils has proved to be very successful, and one of the difficulties in the analysis of chiefly hydrocarbon products is the measurement of the oxygen content. Would Mr Putman like to comment on the feasibility of extending the method of soft X-ray absorption to the measuring of oxygen content? I know that the atomic number of oxygen is not very far removed from that of carbon, but does he think it is worth trying to find just the right wavelength of X-rays for the oxygen atom?

We have been interested for some time in the possible uses of large radiation doses in the field of fuel research, and especially in the effects which ionizing radiation might have on solid catalysts. The common experience is that any effects which are produced are rapidly annealed out at any temperature above room temperature, sometimes in a matter of a few hours, sometimes in a couple of days. We have, however, recently managed to find an effect which persists for at least two weeks at the reaction temperature of 280° C. We have been interested in the Fischer–Tropsch reaction, the reaction for the synthesis of hydrocarbon oils from mixtures of carbon and oxide and hydrogen. We have now found that, using unreduced iron oxide catalysts for this reaction, a dose of the order of $3{\cdot}5 \times 10^7$ roentgen produces an appreciable increase in the activity of the catalyst, which we find to be persistent over at least two weeks. The increase in the activity, in the experiments so far performed, has been up to 50 per cent, and, as far as I am aware, this is the first time that a persistent effect for solid catalysts has been observed. This is interesting in view of Dr Hoare's comments, with which I would agree, that in order to get a significant change in a hydrocarbon, *i.e.* for the change to be of any commercial interest, a very large amount of radiation must be absorbed by the hydrocarbon. However, if one can effect a solid catalyst which will continue in a high state of activity for a long time, then one might make better use of radiation in the production of oils.

J. L. Putman: We do not claim to measure density within 0·1 per cent, but only to be able to detect a change of this magnitude over a relatively short period. This does not place such demands on long-term stability as does measurement within these limits. The accuracy of measurement of the system was estimated at $\pm 0{\cdot}3$ per cent, and it was built to detect changes in the product pumped through a cross-country pipeline.

Density was measured by penetration through a pipe of diameter 10 inches. The source was 300 millicuries of cæsium-137, and two ionization chambers were used as detectors, connected in opposition to provide a null system of measurement. Head amplifiers, directly attached to the ionization chambers, were temperature-controlled with thermostats.

The greater accuracy may be attributed to the use of a larger source with a thicker sample, resulting in a greater proportional change in transmitted radiations for the same change in density. Provided that a sufficiently high flux of radiations is available, ionization chambers are generally capable of more stable operation than Geiger counters, though temperature control is more necessary. An accuracy of 1 to 1½ per cent is quite good when using alcohol-quenched counters as detectors. We have found, however, that halogen-quenched counters have approximately three times better long-term stability of efficiency than alcohol-quenched counters, and it is this stability which limits the accuracy of Geiger counter systems for density or thickness measurements.

I do not think that the oxygen content of hydrocarbons could be usefully measured by X-ray absorption because of the closeness of the atomic numbers of oxygen and carbon, which Dr Gibson points out. If the correct energy could be chosen, so that an X-ray absorption edge falls between carbon and oxygen, there might be some hope of realizing the required contrast in absorption coefficients, but, even so, the method presupposes a source of strictly monochromatic X-rays which would be difficult to obtain from an X-ray tube or by radioactive means.

Dr Gibson's success in irradiating catalysts is very interesting. Certainly an irradiation of small quantities of catalysts, which can then be used in the processing of large quantities of a commercial product, is a technique by which radiation chemistry has the best chance of economic success.

Lord Geddes: Mr Putman has displayed not only the skill of the scientist, but also the skill of a teacher. He has put over a difficult subject in a most extraordinarily clever and interesting way.

A vote of thanks was accorded with acclamation.

CONTRIBUTED DISCUSSION

R. G. Hill: I should like to describe briefly a level gauge using gamma-radiation, the Gagetron, and a recent mishap to it.

Our Thermofor Catalytic Cracker, T.C.C., uses a pellet catalyst based on silica gel, each pellet being approximately ⅛ inch in diameter. Some 250 tons/hour of catalyst are raised 200 ft to the top of the plant by means of an air lift. From the receiving vessel the catalyst passes through the process by gravity. Conditions in the top vessel are severe, because of erosion and the high catalyst temperature, which is of the order of 700° F. A minimum head of catalyst in the vessel is necessary to maintain the seal on the reactor, and as the catalyst is relatively expensive it must not be spilled over the top

of the vessel. To meet these arduous conditions the gamma-ray method of level measurement was selected. The installation has four horizontal tubes at 2 ft vertical spacing extending approximately 2 ft into the vessel, each tube being protected with hard facing and a catalyst retaining trough. Each well contains a steel rod, in the end of which is a gamma-ray source of varying intensity. The sources used have milligram quantities of radium chloride sealed in platinum–iridium tubes, each approximately $\frac{1}{2}$ inch long by $\frac{1}{16}$ inch diameter. External to the vessel is a flameproof housing containing the counter tube and pre-amplifier circuit. The associated counting circuit, amplifier, power pack, and recorder are located in the control room at ground level. The installation is checked each shift and has proved sufficiently accurate and reliable for the recorder to be incorporated in the alarm and shutdown system for the unit.

Some months ago a change in the pattern of catalyst flow in the top receiving vessel caused the falling catalyst to impinge on one of the radium wells. While the hard facing had stood up to three years' normal wear, this concentrated fall eroded the well and eventually released the radioactive source into the catalyst stream. This was first noticed on the recorder, which indicated a sudden large rise in catalyst level. This, of course, was brought about by a decrease in radiation reaching the counter tube.

Some concern was felt at the hazard that could exist to personnel operating the plant.

It was discovered that there is a unit of the Medical Research Council and Ministry of Health known as Radiological Protection Services, whose function it is to ensure good protection of radiological workers in medicine and industry. Tribute must be paid to their speedy and efficient assistance. Under their guidance suitable precautions were adopted, such as careful washing, the use of masks and goggles, and damping of catalyst fines before removal from the unit to prevent any active material becoming airborne and thus being ingested by operatives. When the unit was shut down, R.P.S. again provided assistance in an endeavour to recover the lost sources. A senior member of the refinery staff entered every vessel prior to the maintenance people and checked each piece of plant with a portable monitor. A number of small pieces of radioactive material were recovered, in total rather less than half of that lost. These were embedded in concrete and sunk in deep water from an outgoing tanker. It has been arranged that all catalyst fines, from the date of the loss of the radioactive material and for at least six months, shall be buried at a site which is marked in case it should later prove necessary to carry out excavations on this piece of ground.

Although the plant has been repaired and it is thought unlikely that the catalyst will again fall on the radium wells and cause this gross erosion, the hard facing and protected troughs have all been increased and a pneumatic system installed to provide warning should a pin hole develop in one of the wells.

THE PLUNGER RHEOMETER—LAW OF FLOW FOR A NEWTONIAN LIQUID *

By G. S. SMITH †

INTRODUCTION

THE time of fall of solid bodies of various shapes in a liquid has been made the basis of many different types of viscosity measurements. The falling sphere viscometer is a familiar example. The use of a cylindrical body which was allowed to fall through a liquid in a containing cylinder of radius only slightly greater than that of the falling body was described by Lawaczek,[1] Bridgman,[2] Jobling and Lawrence,[3] Steiner,[4] Amner and Blott,[5] and others.

The plunger rheometer [4] is of this type, but the falling cylinder carries a pan upon which various loads can be placed. It can be used for determining true viscosities in the case of Newtonian liquids and also for studying the behaviour of non-Newtonian liquids. With the former, there is a linear relation between effective load and the reciprocal of the time of fall over a specified distance. With the latter, apparent viscosities under various conditions of loading can be measured and the variation of apparent viscosity with the maximum rate of shear can be assessed. The plunger rheometer can therefore be used to discover if a given liquid shows Newtonian behaviour or, if it does not, to provide a quantitative assessment of its behaviour during various conditions of flow.

The fall of the plunger in the liquid contained in a cylindrical tube causes liquid to be displaced from below the plunger and to flow through the narrow annulus between plunger and tube. This annular space corresponds with the capillary through which liquid flows in a capillary viscometer.

A determination of the viscosity in absolute units of a Newtonian liquid can be carried out with the plunger rheometer if the instrument is calibrated against a fluid of known viscosity. The flow can, however, be treated mathematically as with a capillary viscometer in the way indicated below, and an absolute determination of viscosity can be calculated from the dimensions of the apparatus, the load, and the rate of fall of the plunger. Apparent viscosity determinations of non-Newtonian liquids depend on viscosity determinations of Newtonian liquids. Hence the conditions of flow for the latter are fundamental.

In the mathematical treatment of the problem due to Lawaczeck,[1] the flow of liquid through the annulus is considered as equivalent to flow between rectangular parallel plates, one of which is moving at constant speed in a plane at a distance from the other equal to the width of the annulus. The width of each plate is taken to be the length of the circumference of the falling cylinder, and the effective length is that of the cylinder. The viscosity of the liquid is calculated from the formula

$$\eta_1 = \frac{\delta^3 d(\gamma_1 - \gamma_2)}{v\{3(d + 2\delta)^2 + 4\delta^2\}}$$

where d is the diameter of the falling cylinder, δ is the width of the annulus, v is the rate of fall of the cylinder, γ_1 is the specific gravity of the falling cylinder, and γ_2 is the specific gravity of the liquid. By assuming 2δ can be neglected in comparison with d, Lawaczeck obtains an approximate value for η_1

$$\eta_1 \approx (\gamma_1 - \gamma_2)\frac{\delta^3}{3vd}$$

In this treatment any effects that may be due to the cylindrical nature of the boundary surfaces of the liquid are not taken into account. Other workers appear to have made the same assumptions as Lawaczeck. The formula given by Amner and Blott[5] as applicable to their plunger viscometer is equivalent to Lawaczeck's approximate formula with d replaced by $d + 2\delta$.

THEORETICAL

To obtain equations for the law of flow of a Newtonian liquid in a cylindrical plunger rheometer, the same assumptions are made as for flow in a capillary, *e.g.* that the flow is parallel with the axis, that there is no slip at the walls of the vessel, etc., and, in addition, that the "head resistance" due to the form of the stream lines at the ends of the cylinder can be neglected if the cylinder is long compared with its diameter, and the width of the annulus is small.

The problem to be solved is therefore basically that of flow through an annulus, the inner wall of which is moving relatively to the outer.

Let the radii of the plunger and containing cylinder be a_1 and a_2 respectively, and let l be the length of the cylinder, which is supposed to be totally submerged in the liquid. Because of the fall of the cylinder a pressure is exerted on the liquid, causing it to flow up

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through the annulus. Let the pressure difference in the liquid between the bottom and the top of the annulus when a steady flow has been attained be p_1. This includes the hydrostatic pressure difference p_0 due to the difference in depth of the two levels below the surface of the liquid.

Consider the forces acting on a thin cylindrical shell of liquid co-axial with the plunger and outer cylinder and situated in the space between them. Let the radius of the inner surface be r, that of the outer surface be $r + dr$, and let the length be l. Let v be the velocity of the liquid at the inner surface; v is constant throughout the length of this surface. There is a shear force F, or $2\pi rl\eta\frac{dv}{dr}$, where η is the viscosity and $\frac{dv}{dr}$ is the rate of change of velocity with r, on the inner surface, and a shear force $F + \frac{dF}{dr}dr$ on the outer surface in the opposite direction. The other forces on the shell of liquid are those due to the pressure p_1 and the force of gravity on the liquid. The weight of liquid in the shell is $2\pi rdrl\rho g$, where ρ is the density of the liquid, and this by elementary hydrostatic principles can be equated to the difference in the ordinary hydrostatic pressure forces at the top and bottom of the shell, *i.e.* to $2\pi rp_0dr$, where p_0 is the hydrostatic pressure difference.

The force due to the pressure p_1 is $2\pi rdrp_1$, and this acts in opposition to the force of gravity.

With uniform motion the sum of the forces on the shell of liquid must be zero. Hence

$$\begin{aligned}\frac{dF}{dr}dr &= -2\pi rdrp_1 + 2\pi rdrp_0\\ &= -2\pi rdr(p_1 - p_0)\\ &= -2\pi rdrp,\end{aligned}$$

where $p = p_1 - p_0$.

or $$\frac{d}{dr}\left(r\frac{dv}{dr}\right)dr = -\frac{p}{\eta l}rdr$$

Integrating, one has

$$r\frac{dv}{dr} = -\frac{pr^2}{2\eta l} + C,$$

where C is a constant,

or $$\frac{dv}{dr} = -\frac{pr}{2\eta l} + \frac{C}{r} \quad . \quad . \quad . \quad (1)$$

Integrating again, one has

$$v = -\frac{pr^2}{4\eta l} + C\log r + D \quad . \quad (2)$$

where D is another constant.

The volume of liquid passing through the shell between cylinders of radii r and $r + dr$ in unit time is $2\pi rdr.v$. Hence the total volume of liquid passing through the annulus in unit time is

$$\int_{a_1}^{a_2} 2\pi rv.dr$$

or $$\pi\int_{a_1}^{a_2}\left(-\frac{pr^3}{2\eta l} + 2Cr\log r + 2Dr\right)dr$$

$$= \pi\left[-\frac{pr^4}{8\eta l} + Cr^2\log r - \frac{Cr^2}{2} + Dr^2\right]_{a_1}^{a_2}$$

$$= -\frac{\pi p}{8\eta l}(a_2^4 - a_1^4) + \pi\{a^2{}_2(C\log a_2 + D) - a_1^2(C\log a_1 + D) - \frac{C}{2}(a_2^2 - a_1^2)\} \quad . \quad (3)$$

Now $v = 0$ when $r = a_2$, and $v = -V$ when $r = a_1$, where V is the rate of fall of the plunger.

Substituting these values in (2), one has

$$\frac{pa_2^2}{4\eta l} = C\log a_2 + D \quad . \quad . \quad . \quad (4)$$

$$-V + \frac{pa_1^2}{4\eta l} = C\log a_1 + D \quad . \quad . \quad (5)$$

Hence the total volume passing through the annulus in unit time (see (3)) is

$$-\frac{\pi p}{8\eta l}(a_2^4 - a_1^4) + \pi\left\{\frac{pa_2^4}{4\eta l} - \frac{pa_1^4}{4\eta l} + Va_1^2 - \frac{(a_2^2 - a_1^2)\left(\frac{p(a_2^2 - a_1^2)}{4\eta l}\right) + V}{2\log a_2/a_1}\right\}$$

$$= \frac{\pi p}{8\eta l}(a_2^4 - a_1^4) - \frac{\pi p(a_2^2 - a_1^2)^2}{8\eta l\log a_2/a_1} + \pi Va_1^2 - \frac{\pi V(a_2^2 - a_1^2)}{2\log a_2/a_1}$$

But the total volume passing in unit time must also be the volume of fluid displaced by the plunger in unit time, *i.e.* πa_1^2V.

Hence

$$p(a_2^4 - a_1^4)\log\frac{a_2}{a_1} - p(a_2^2 - a_1^2)^2 = 4\eta lV(a_2^2 - a_1^2)$$

$$\therefore \quad \eta = \frac{p}{4lV}\{(a_2^2 + a_1^2)\log\frac{a_2}{a_1} - (a_2^2 - a_1^2)\} \quad (6)$$

$$= \frac{p\theta}{4lV}, \text{ say,} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where $\theta = (a_2^2 + a_1^2)\log\frac{a_2}{a_1} - (a_2^2 - a_1^2)$ . . (8)

The rate of shear, $\frac{dv}{dr}$, at the plunger surface is given by (1) with $r = a_1$ and C derived from (4) and (5).

$$\left(\frac{dv}{dr}\right)_{r=a_1} = \frac{-pa_1}{2\eta l} + \frac{C}{a_1}$$

$$C = \left(\frac{p(a_2^2 - a_1^2)}{4\eta_i l} + V\right)\frac{1}{\log a_2/a_1}$$

$$= \left(\frac{p(a_2^2 + a_1^2)\log a_2/a_1}{4\eta_i l} - V + V\right)\frac{1}{\log a_2/a_1} \quad \text{from (6)}$$

$$= \frac{p(a_2^2 + a_1^2)}{4\eta_i l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Hence $\left(\frac{dv}{dr}\right)_{r=a_1} = \frac{p}{4la_1\eta_i}(a_2^2 - a_1^2) \quad . \quad . \quad (10)$

The shear stress at the plunger surface is, by definition,

$$\eta_i\left(\frac{dv}{dr}\right)_{r=a_1} \quad \text{or} \quad \frac{p}{4la_1}(a_2^2 - a_1^2).$$

Now consider the forces on the plunger. Let M_1 be the total mass of the plunger. The weight $M_1 g$ is balanced by the shear force over the vertical sides of the plunger and the difference in the pressure force at the bottom and top of the cylinder. The shear force over the area $2\pi a_1 l$ is $\frac{\pi p}{2}(a_2^2 - a_1^2)$ and the resultant pressure force over the area πa_1^2 is $\pi p_1 a_1^2$. Hence

$$M_1 g = \frac{\pi p}{2}(a_2^2 - a_1^2) + \pi p_1 a_1^2$$

$$= \frac{\pi p}{2}(a_2^2 - a_1^2) + \pi(p + p_0)a_1^2$$

$$= \frac{\pi p}{2}(a_2^2 + a_1^2) + \pi p_0 a_1^2$$

Since the plunger is submerged, its apparent weight is reduced because of buoyancy. If Mg is the corrected weight one has

$$Mg = M_1 g - \pi a_1^2 p_0$$

$$= \frac{\pi p}{2}(a_2^2 + a_1^2)$$

$$p = \frac{2Mg}{\pi(a_2^2 + a_1^2)} \quad . \quad . \quad . \quad (11)$$

Substituting for p in (7), one has

$$\eta_i = \frac{Mg\theta}{2\pi l V(a_2^2 + a_1^2)} \quad . \quad . \quad (12)$$

where all the quantities can be found experimentally.

The rate of shear at the plunger surface

$$= \frac{p}{4la_1\eta_i}(a_2^2 - a_1^2), \text{ see (10)}$$

$$= \frac{V(a_2^2 - a_1^2)}{a_1\theta}, \text{ from (7)}, \quad . \quad . \quad (13)$$

The shear stress at the plunger surface

$$= \frac{p}{4la_1}(a_2^2 - a_1^2)$$

$$= \frac{Mg(a_2^2 - a_1^2)}{2\pi l a_1(a_2^2 + a_1^2)}, \text{ from (11)} \quad . \quad (14)$$

The variation of rate of shear across the annulus from $r = a_1$ to $r = a_2$ is given by (1) and (9)

$$\frac{dv}{dr} = \frac{p}{4l\eta_i r}(a_2^2 + a_1^2 - 2r^2)$$

$$= \frac{V}{r\theta}(a_2^2 + a_1^2 - 2r^2), \text{ from (7)}$$

Thus its numerical value varies with increase of r from $\frac{V}{a_1\theta}(a_2^2 - a_1^2)$ at the plunger surface, through zero at $r = \sqrt{\frac{a_2^2 + a_1^2}{2}}$, to $\frac{V}{a_2\theta}(a_2^2 - a_1^2)$ at the surface of the containing vessel. The greatest value is thus at the plunger surface and (13) represents the maximum rate of shear.

The quantity θ which occurs in the expressions for η_i and $\frac{dv}{dr}$ is the difference of two relatively large quantities (see (8)) which are nearly equal. To obtain an approximation of greater use for calculation purposes one can take

$$\log\frac{a_2}{a_1} = \log\frac{a_1 + d}{a_1} = 2\left\{\frac{d}{2a_1 + d} + \frac{1}{3}\left(\frac{d}{2a_1 + d}\right)^3 + \quad\right\}$$

and ignore all terms in the series containing powers of d greater than the third, in view of the fact that $d \ll a_1$.

$$\therefore \quad \log\frac{a_2}{a_1} \approx \frac{8[(a_1 + d)^3 - a_1^3]}{3(2a_1 + d)^3}$$

and

$$(a_2^2 + a_1^2)\log\frac{a_2}{a_1} \approx \frac{8(2a_1^2 + 2a_1 d + d^2)(2a_1 + d)[(a_1 + d)^3 - a_1^3]}{3(2a_1 + d)^4}$$

Now $\dfrac{(2a_1 + d)^4}{2a_1^2 + 2a_1 d + d^2} = 8a_1^2 + 8a_1 d + \dfrac{d^4}{2a_1^2 + 2a_1 d + d^2}$

by actual division

$\approx 8a_1(a_1 + d)$, since the last term is negligible.

$$\therefore \quad (a_2^2 + a_1^2)\log\frac{a_2}{a_1} \approx \frac{(2a_1 + d)[(a_1 + d)^3 - a_1^3]}{3a_1(a_1 + d)}$$

$$= \frac{(a_2 + a_1)(a_2^3 - a_1^3)}{3a_1 a_2}$$

Hence since $\theta = (a_2^2 + a_1^2)\log\frac{a_2}{a_1} - (a_2^2 - a_1^2)$

one has $\quad \theta \approx \frac{(a_2 + a_1)(a_2^3 - a_1^3)}{3a_1 a_2} - (a_2^2 - a_1^2)$

$$= \frac{(a_2^2 - a_1^2)(a_2 - a_1)^2}{3a_1 a_2}$$

On substituting this value of θ in (12), (13), etc., one has

$$\eta_i = \frac{Mg(a_2^2 - a_1^2)(a_2 - a_1)^2}{6\pi l V a_1 a_2(a_2^2 + a_1^2)}$$

$$\text{Rate of shear at plunger surface} = \frac{3Va_2}{(a_2 - a_1)^2}$$

$$\text{Rate of shear at vessel surface} = \frac{3Va_1}{(a_2 - a_1)^2}$$

EXAMPLE OF THE USE OF THE FORMULÆ

With a rheometer in which $a_2 = 1{\cdot}27$ cm, $a_1 = 1{\cdot}118$ cm, and $l = 8{\cdot}7$ cm one has $\theta = 0{\cdot}00198$.

Hence $\eta = 0{\cdot}0124 \dfrac{M}{V}$ poises (from (12))

Max rate of shear $= 164\ V$ sec^{-1} (from (13))

Shear stress on plunger $= 2{\cdot}044\ M$ dynes/sq. cm. from (14)).

ACKNOWLEDGMENT

Acknowledgment is made to the Controller, H.M. Stationery Office, for permission to publish this paper.

References

[1] Lawaczeck, F. *Zeitschrift des Vereines deutsches Ingenieure*, 1919, **63**, 677–82.
[2] Bridgman, P. W. *Proc. Amer. Acad.*, 1926, **61**, 57.
[3] Jobling, A., and Lawrence, A. S. C. *Proc. Roy. Soc.*, 1951, **206A**, 257–74.
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SCUFFING TESTS FOR GEAR OILS

For many years now the IAE 3¼-inch centre gear machine has been in use in several laboratories in Britain, and in some laboratories abroad, for determination of the load-carrying capacity of gear oils under conditions of comparatively low sliding velocity. The operation of this rig, which consists basically of two pairs of spur gears loaded back to back, was fully described in a paper given by the Mechanical Tests of Lubricants Panel of Standardization Sub-Committee No. 5[1] at the Symposium on Gear Lubrication in February 1952, and was also referred to in other papers given at the same Symposium.[2–4]

Extensive correlation work by several laboratories then indicated that the machine was a satisfactory instrument for rating oils intended for use in all spur gearing, including the maximum duties which could be envisaged. It should be pointed out that the machine was never intended to rate such special-purpose lubricants as those used with worm or hypoid gears.

Since 1952 a considerable amount of development work and correlation work has been carried out on the rig, and recently both the Admiralty and the Air Ministry have indicated their wish for a published standard method of test for the operation of the rig. As a result of work carried out by laboratories associated with the Mechanical Tests of Lubricants Panel now operating under Sub-Committee No. 6, a standard method has been drafted which is acceptable to all laboratories and to both Government bodies concerned, and which covers operation of the rig under set conditions at 2000, 4000, and 6000 rev/min. This method has been accepted by the Standardization Committee for publication in the 17th Edition of "Standard Methods for Testing Petroleum and Its Products" as a Tentative Standard Method, and will appear as IP 166/58T. The proposed method is as follows:

SCUFFING TEST OF GEAR OIL
IP 166/58T

Introduction

1. Scuffing is a particular type of deterioration of metallic surfaces in sliding contact, generally assumed to be due to the local welding of parts of the opposing surfaces. A typical scuffing failure is shown in Fig 1. Scuffing may be preceded by polishing, and although the load at which this occurs is customarily noted, it is not considered as the failure load. Another type of failure occasionally experienced is scoring, and a typical scoring failure is shown in Fig 2. In the following test method, scoring is taken to be equivalent to scuffing. Pitting may be encountered at high loads, but under the test conditions specified these loads would be almost sufficient to cause tooth breakage. In a very limited number of cases when pitting does occur, it is not regarded as oil failure due to scuffing.

Scope

2. This method of test may be used to evaluate the anti-scuffing qualities of gear oils when used to lubricate steel/steel

straight-spur gears. The results are generally assumed to be applicable also to steel/steel helical gears.

Outline of Method

3. A special gear rig is operated for a series of short periods, at increasing loads, the oil under test being used to lubricate the test gears. The performance of the oil is evaluated by the load at which scuffing or scoring of the gear faces occurs.

Apparatus

4. (*a*) *Test Rig*—a power-circulating gear test rig of the type developed by the Institution of Automobile Engineers employing special test gears. It is known as the IAE 3¼-inch Centres Gear Lubricant Testing Machine. The rig is described in Appendix A.

(*b*) *Test Gears*—as described in Appendix A.

Materials

5. *White Spirit*—conforming to BS 245 : 1956.

Preparation of Apparatus

6. (*a*) Follow the makers' "Operating and Servicing Instructions" for the general operation of the machine.

(*b*) Before commencing a test on a new lubricant, remove and discard the paper filter-element and flush the test oil system through twice for 15 minutes, first with the white spirit at room temperature and then with the test lubricant at the test temperature (Table I). Switch off the heater, allow the oil to drain for 15 min during which time insert a new paper filter element and refill with 1 IG of the test lubricant.

(*c*) When repeating tests on the same lubricant, the oil must be changed, but the flushing procedure may be omitted. Change the filter element for every other test.

(*d*) Thoroughly cleanse the gears in the white spirit before fitting them in the machine and *immediately prior to the test*.

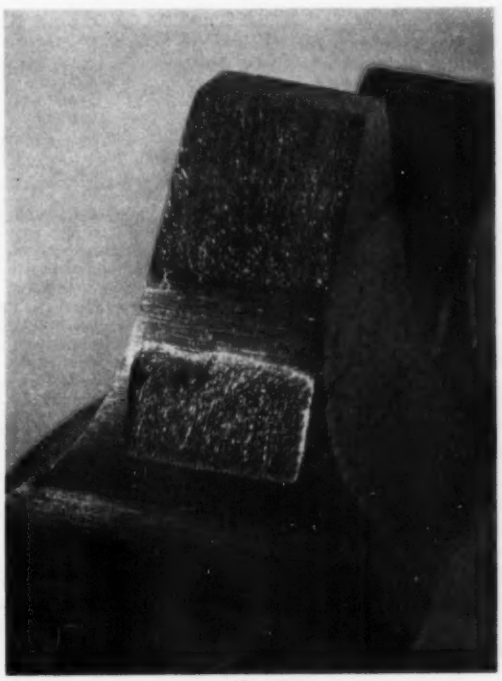

Fig 1

TYPICAL SCUFFED TOOTH

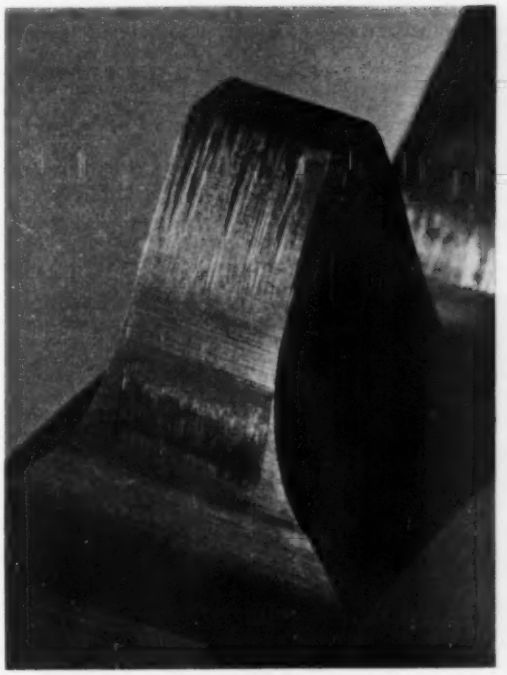

Fig 2

TYPICAL SCORED TOOTH

Procedure

7. (*a*) The three sets of nominal conditions to be used for scuffing tests are given in Table I.

Table I

Nominal conditions	A	B	C
Pinion speed, rev/min	2000	4000	6000
Test oil temperature, °C	60	70	110
Test oil temperature, °F	140	158	230
Test oil flow, I.pt/min	½	1	1
Initial load (18-inch lever arm), lb	10	10	10
Load increment	5	5	5
Test period, min	5	5	5
Rest period (time between tests), min	5	5	5

(*b*) Fit the clean selected test gears.

(*c*) Switch on the heater and test oil pump and allow the oil to circulate at the correct flow rate until the temperature remains constant at the selected value (Table I).

(*d*) Apply an initial load of 10 lb by the application of the standard 18-inch lever arm and weight carrier without added weights.

(*e*) Operate the machine under the appropriate conditions for 5 min (Table I).

(*f*) Stop the machine and allow it to remain at rest for 5 min, during which period examine the teeth of the test gears for evidence of scuffing or scoring (see Figs 1 and 2).

(*g*) Visual inspection will show one of the following conditions of the gear teeth:

(i) no scuffing has occurred;

(ii) scuffing has occurred only in approach or recess (see para (*k*));

(iii) scuffing is complete as illustrated in Figs 1 or 2.

(*h*) If no scuffing has occurred increase the lever load by the addition of a 5-lb weight and operate the machine for a further 5 min and repeat procedure (*f*).

(*i*) Repeat the 5-min operation and the 5-min rest period with increasing loads at increases of 5 lb until the teeth are found to be scuffed or scored.

(*j*) The onset of scuffing may be indicated by the following:

(i) change in note of the noise of the rig;

(ii) appearance of smoke in the test box;

(iii) a sudden increase in the current taken by the driving motor;

(iv) a sudden increase in the temperature of the oil emerging from the contact zone (as indicated by the thermocouple if this is fitted to measure the contact zone temperature).

In such cases the rig may be stopped before the 5 min (para (*e*)) are completed in order to avoid the possibility of excessive damage to the gears occurring. It must be emphasized, however, that these changes are not always coincident with the onset of scuffing, and the criterion in every case is the actual occurrence of scuffing as detected visually.

(*k*) Scuffing of the teeth may occur at a certain load in "approach," *i.e.* as the teeth first come into mesh (which affects the dedenda of the driving and the addenda of the driven gear teeth) and at another load in "recess," *i.e.* as the teeth go out of mesh (which affects the addenda of the driving and the dedenda of the driven gear teeth).

(*l*) If on inspection scuffing is found to have occurred only in approach or recess, record the load and continue the test until scuffing is complete as illustrated in Fig 1 or 2. Record the final load.

(*m*) If an inspection scuffing is complete as illustrated in Fig 1 or 2, record the load.

(*n*) If the machine has been stopped before the end of the 5-min period as described in para (*j*) and no scuffing has occurred, complete the 5-min run and continue the test according to para (*h*), (*i*), (*l*), (*m*).

(*o*) Carry out a total of four tests under the chosen set of conditions (Table I) using one face of four pairs of gears on any one lubricant.

Calculation and Reporting

8. Report the scuffing load for each of the four tests, both in approach and recess, separately. When scuffing is complete at one loading, report this as the loading both in approach and recess.

From the eight results obtained, calculate the arithmetic mean to the nearest whole number.

Report the eight results and their mean as the Scuffing Test, IP 166, condition A, B, or C (Table I) as appropriate.

Precision

9. The precision of the method has not been established.

Appendix I

Apparatus

A1. (*a*) *Gear Test Rig*—a power-circulating type gear test rig of the type developed by the Institution of Automobile Engineers employing special test gears. It is known as the IAE 3½-inch Centres Gear Lubricant Testing Machine. The sole authorized manufacturer of the rig is W. E. Sykes Ltd, Staines, Middlesex, England.

The rig consists of two gear boxes, containing respectively the test gears and the "power-return" gears, coupled in parallel by two torsion shafts, one of which carries a split coupling so that torque can be applied to the system. Loads up to 200 lb may be applied on the loading lever, corresponding to 300 lb ft torque and approximately 12,000 lb/inch tooth face pitch-line loading.

The apparatus shall have separate oil systems for the test gears and the power-return gears. The test oil system shall include means of controlling both the flow and temperature of the oil, while both magnetic and paper element filters shall be fitted. The temperature of the oil shall be controlled by a bulb type indicator controller, the sensitive element of which shall be located immediately prior to the oil jet.

(*b*) *Magnetic Filter*—a Phillips Type E 7715 filter.

(*c*) *Paper Element Filter*—a Purolater "Micronic" MF 2604 filter fitted with an MF 26A element.

(*d*) *Oil Feed Jet*—the gears shall be fed with oil by an 0·8-mm dia jet (Sykes Drg No. AM 37077) directed vertically downwards towards the meshing point of the gears.

If the pinion rev/min is n and the load on the standard 18-inch lever arm is W lb, then for the standard 15/16 ratio gears the following apply:

Pitch-line velocity, ft/min	$= 0{\cdot}82\,n$
Maximum sliding velocity, ft/min	$= 0{\cdot}39\,n$
Pitch-line tooth loading lb/min	$= 61{\cdot}0\,W$
Horsepower	$= 0{\cdot}00029\,W\,n$

A2. *Test Gears*—brief details are given in Table II and full details in Sykes Drg Nos. AM 13678E, AM 13677E and BM 13889. Authorized suppliers are W. E. Sykes Ltd, Staines, Middlesex, England, and British Gear Grinding and Manufacturing Company Ltd, Standard Road, Park Royal, London, N.W.10, England.

Table II

Details of Test Gears

Number of teeth	15	16
Working pitch-circle dia, inches	3·145	3·355
Base circle dia, inches	2·819	3·007
Working pressure angle	26° 19′	26° 19′
Diametral pitch	4·769	4·769
Face width, inch	0·188 ± 0·001	0·188 ± 0·001
Tip relief, inch	0·0003 ± 0·0001	0·0005 ± 0·0001

The gears shall be made in EN 34·2% nickel–molybdenum steel, carburized, hardened, and ground conforming to BS 971 : 1950. Either face may be used for test. Scuffed, scored, or pitted gears must not be reground and re-used.

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1 *J. Inst. Petrol.*, 1952, **38**, 705–11.

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MEASURING THE PRECISION OF TEST METHODS *

By E. A. FIELD †

In the petroleum industry, product quality is of prime importance and consistent product quality can be achieved only by constant checking with the aid of standard test methods. In applying these, it is clearly important to know how reliable the results are, and most of the IP and ASTM methods possess a section entitled " Precision," containing figures described as " Repeatability " and " Reproducibility." These figures are now being assessed statistically and the procedure by which these figures are derived by the Statistical Sub-Committee of the Institute of Petroleum is described in simple terms in this note.

For any given test method, duplicate determinations of the same property will not usually give precisely the same answer. Sometimes a large part of the difference may be due to incompleteness in the instructions of the test-method, but even after this source of error has been removed it is still unlikely that the repeat results will be exactly the same. The extent to which the two results differ—or in other words, the degree of variability—will, in general, depend on the conditions under which the test was repeated, when the test was repeated, and by whom. A measure of this variability ought to be obtained when every new test method is evaluated to find out what precision can be expected of it in practice.

Because it would be exceedingly complicated to measure the degree of variability for every possible combination of operating conditions, it is usual to choose two, called the Repeatability (R_T) and the Reproducibility (R_D). These may be defined as follows :

(a) *Repeatability is a quantitative measure of the variation that a single operator in any one laboratory would show in obtaining successive repeat results with the same apparatus. It is defined as the difference between any two single results that would be exceeded in the long run in only one case in twenty when the normal and correct operation of the test method is followed.*

(b) *Reproducibility is a quantitative measure of the variability associated with different operators working in different laboratories, each obtaining single results on identical test material. It is defined as the difference between any two such single and independent test results that would be exceeded in the long run in only one case in twenty with the normal and correct operation of the test method.*

The appropriate values of repeatability and reproducibility are determined for many IP and ASTM methods by statistical methods, and these are then shown in the section entitled " Precision."

In general, there are five main ways in which the reliability of test results can be affected : variation can be due to sampling or apparatus, operator techniques or laboratory conditions, or even the time at which the test is made. Even though the test is made using only one set of apparatus, the results may still vary, though usually the size of this variation will be less than that obtained using two different sets of apparatus. The first (and smaller) variation can be called the " within apparatus " variation, and then the latter (and larger) variation becomes the " between apparatus " variation. The size of the " between " variation is influenced by all the factors contributing to the " within " variation, plus those factors arising specifically from the use of more than one apparatus. This idea of " within " and " between " variation also applies to the other sources of variation—sampling, operator, and so on. Using this notation of " within " and " between," the sources of variation contributing to repeatability and reproducibility can thus be tabulated :

	Source of Variation				
	Sampling	*Apparatus*	*Operator*	*Laboratory*	*Time*
Repeatability	Between	Within	Within	Within	Within
Reproducibility	Between	Between	Between	Between	Between

Thus, an operator would use repeatability to check his own precision in carrying out a test-method, whereas comparison of test results obtained in several laboratories would be made with the aid of reproducibility.

To establish the proper values for repeatability and reproducibility for a new test-method, one or more samples of the appropriate product are circulated, with testing instructions, among several laboratories. The work is planned to ensure that the samples are repeat-tested under the proper conditions associated with repeatability and reproducibility so that these may be estimated correctly. The analysis of the test results then takes the following form :

(i) conversion of the original data into a more convenient form if necessary ;

(ii) rejection of rogue results ;

(iii) calculation of R_T and R_D using a standard statistical procedure.

The first part is concerned with converting the original data into a more useful form because, although the test produced results in practical units, these are not necessarily the best for the analysis. Thus, if the

* MS received 15 March 1957.

† Esso Research Ltd.

variability became larger as the results themselves became larger, it might be necessary to use logarithms. When the analysis is complete, the results can be changed back into their original units if that is preferred.

As is well known, in any experimental work it is often difficult to avoid "rogue" results. Rogue results, as their name implies, appear to have an erratic variability not present among the rest of the results. Rogue results may be present for any of the following reasons:

(*a*) an individual determination is spoilt without the knowledge of the operator;

(*b*) all determinations from a particular laboratory may be in error because their sample became contaminated or their instrument is unknowingly biased;

(*c*) the variation of results may be excessive in one laboratory due to misinterpretation of the directions or to general carelessness.

The theory of identifying rogue results is still very much in its infancy. The only safe and good basis for detecting an apparently discordant result is to try to trace it back to some definite error. In the evaluation of a test method we are generally concerned with two types of rogue behaviour. One is the occurrence of an odd result, known as an "outlier," which differs widely from its companions; the other occurs when the variations within one group of results are widely different from those within the remainder.

Several tests have been suggested for dealing with the situation where one result appears to be markedly different from the other results of the same set. Justification for rejecting "outliers" is made on the ground that so large a difference between one result and the others of the set would not occur in the normal course of events.

The second type of rogue behaviour is concerned not with the actual values of the results but with their variability. If for some reason the results from one laboratory are more scattered than the rest, then it is clearly necessary to find out why this has happened and if necessary re-check the results on a fresh sample. If rogue results were left in the data, false estimates of R_T and R_D would be obtained, and so they are usually eliminated before any further analysis is attempted.

The final step in the analysis is the determination of variability. By means of an algebraic process, the main factors which affect the reliability of the test method can be taken into account, thereby enabling unbiased estimates of the repeatability and reproducibility to be made. This is a standard mathematical procedure which need not concern us here.

In practice, limited resources in man-power and time restrict the number of results that can be made available for assessing the R_T and R_D of a particular test method. Moreover, it often happens that not all the results planned are eventually obtained. Both these practical aspects of the evaluation require that compromises be made in carrying out the analysis.

In the foregoing, details of all the statistical techniques that are commonly used for this work have been omitted. This has been done for two reasons; first, because a thorough explanation of any one of the techniques would itself involve a very lengthy exposition, and secondly, because it would be a very lengthy task to cover all possible circumstances. However, details of the statistical techniques can be found in such books as "Statistical Methods in Research and Production," ed. O. L. Davies, 1947.

This discussion has been restricted to the problem of determining the precision of a test method, and little has been said about the related problem of using measures of precision once they have been determined. The problem of control of product quality by specifications based on test methods is an example of this, and a paper on the subject has been presented to the Institute of Petroleum (*J. Inst. Petrol.*, 1956, **42**, 105). Reference should also be made to the Appendix E on the Interpretation and Recommended Usage of Precision Data in "Standard Methods."

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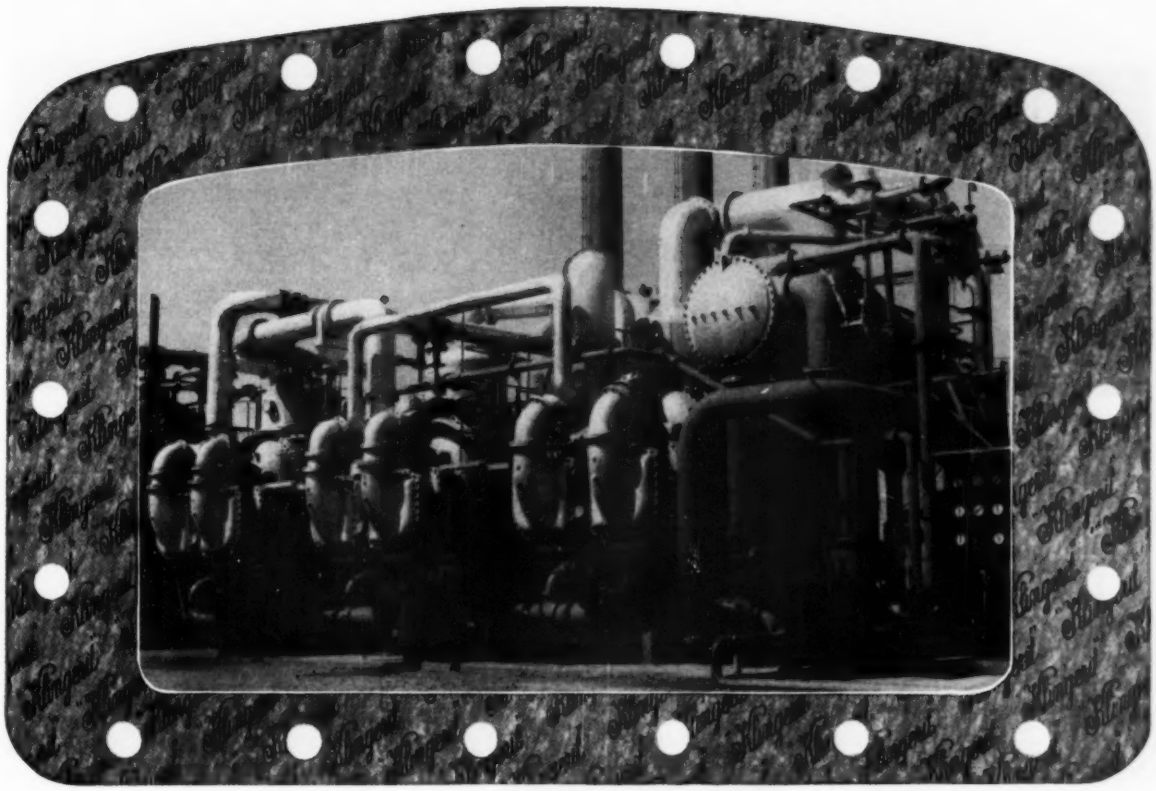

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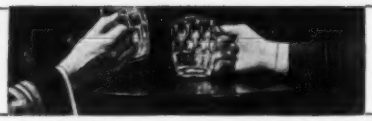

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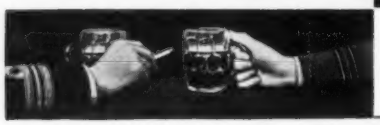

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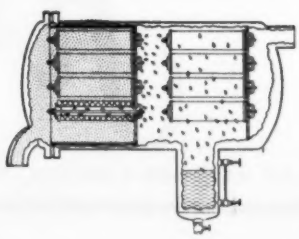

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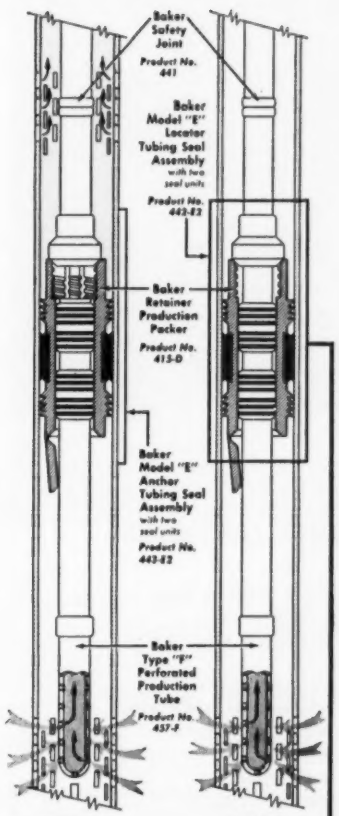
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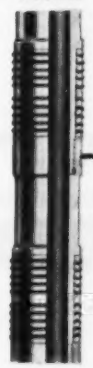

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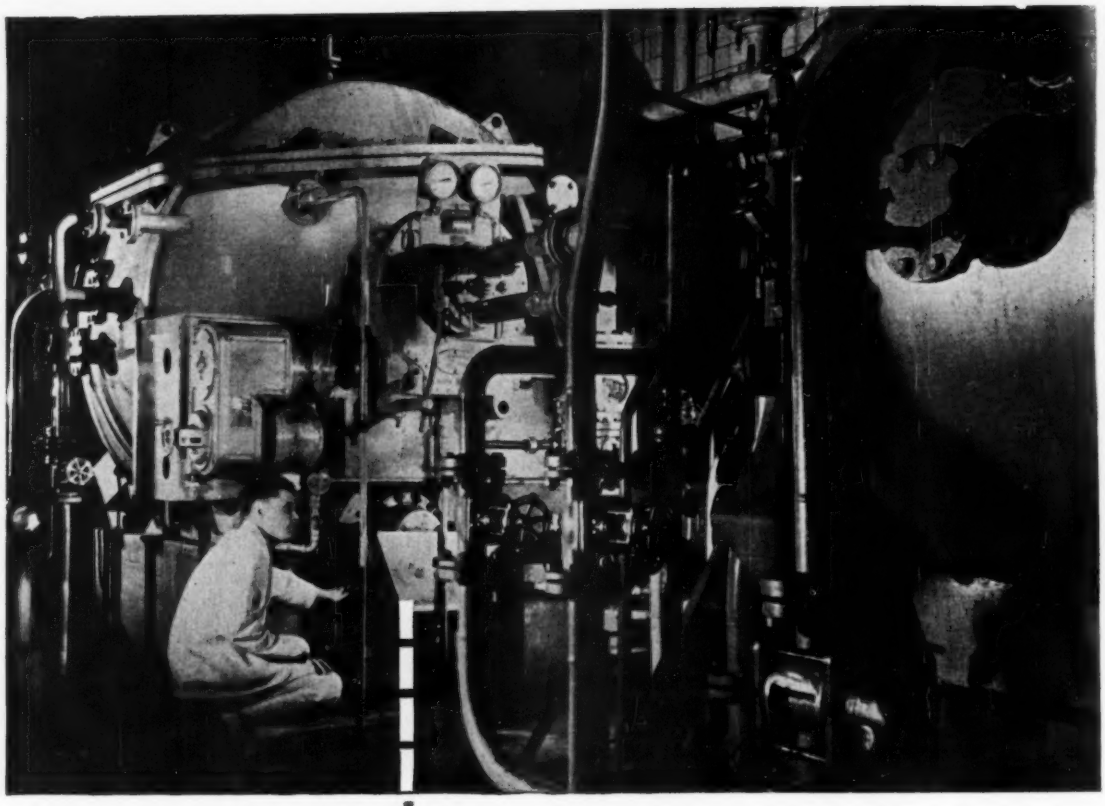

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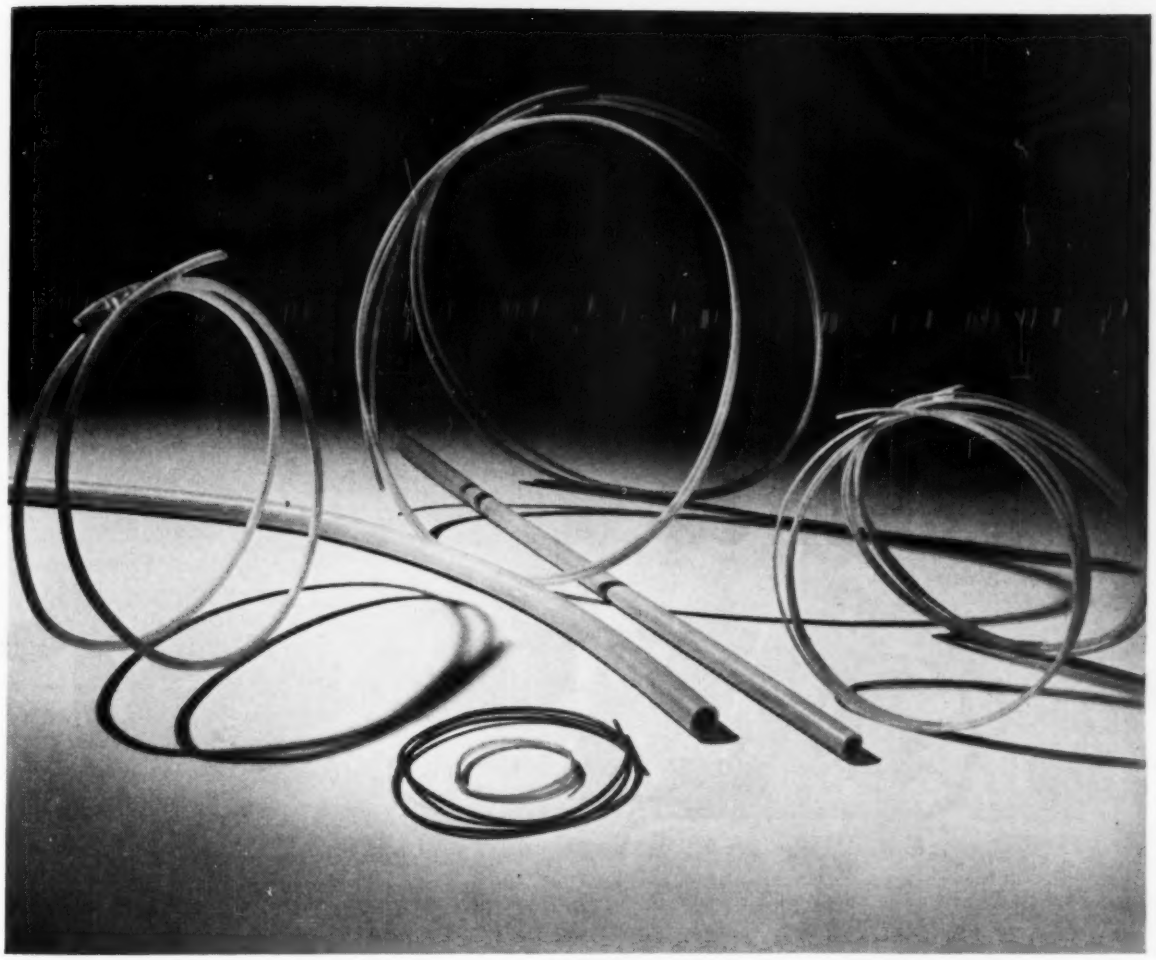

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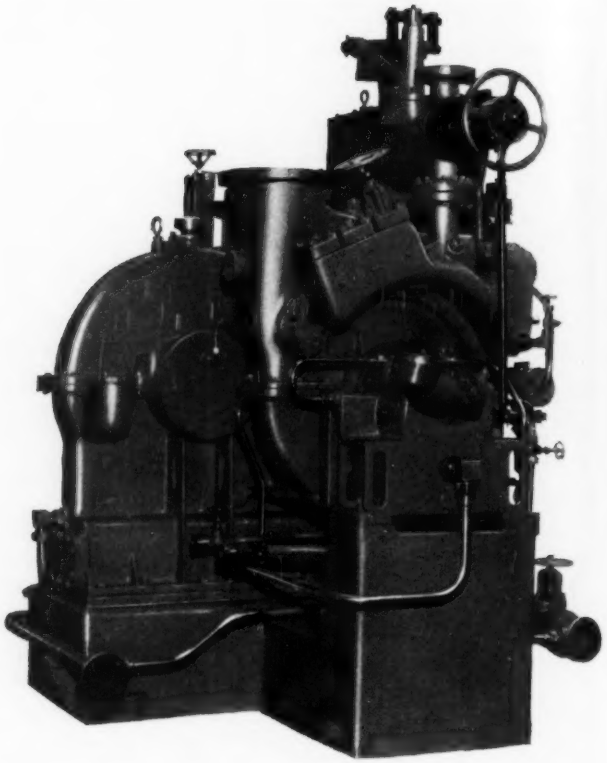

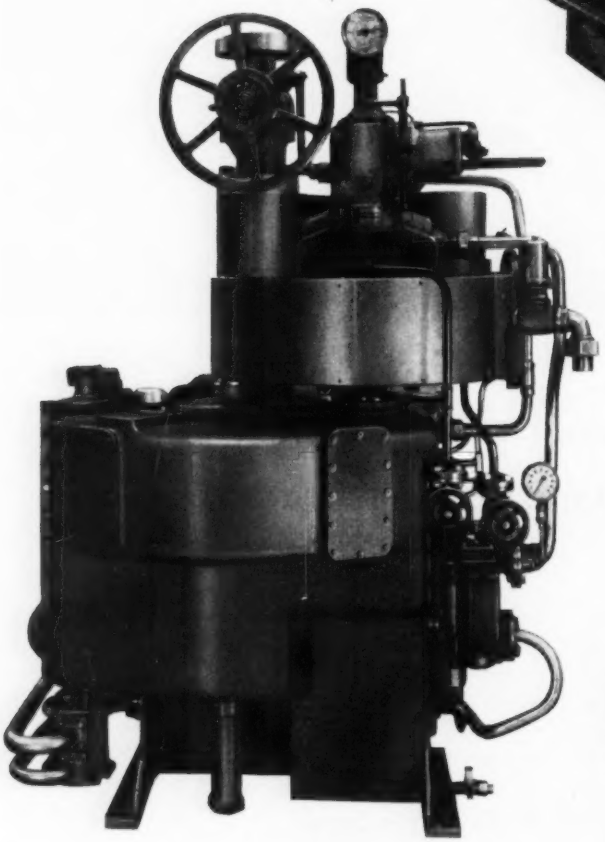

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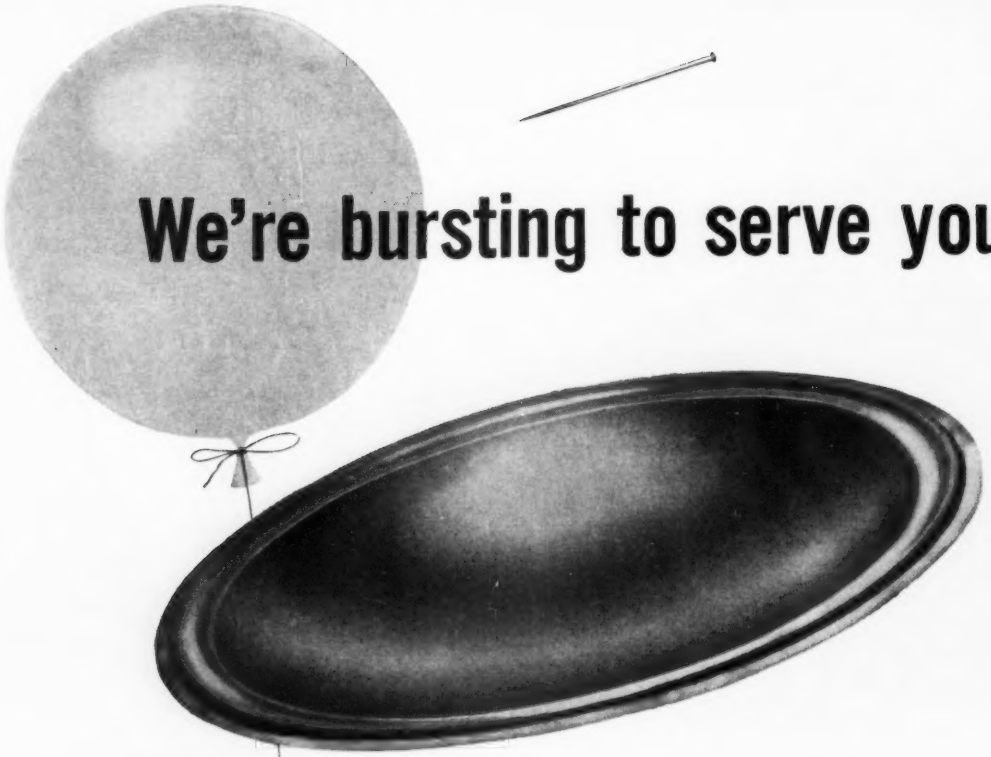

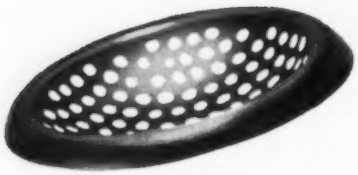

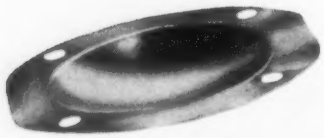

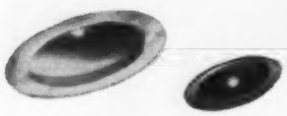

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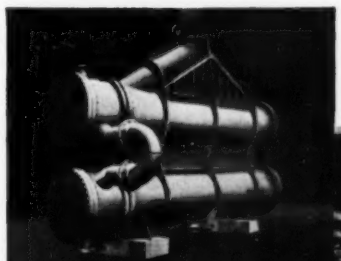
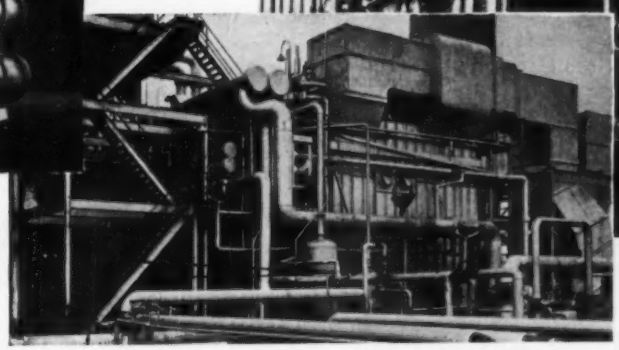
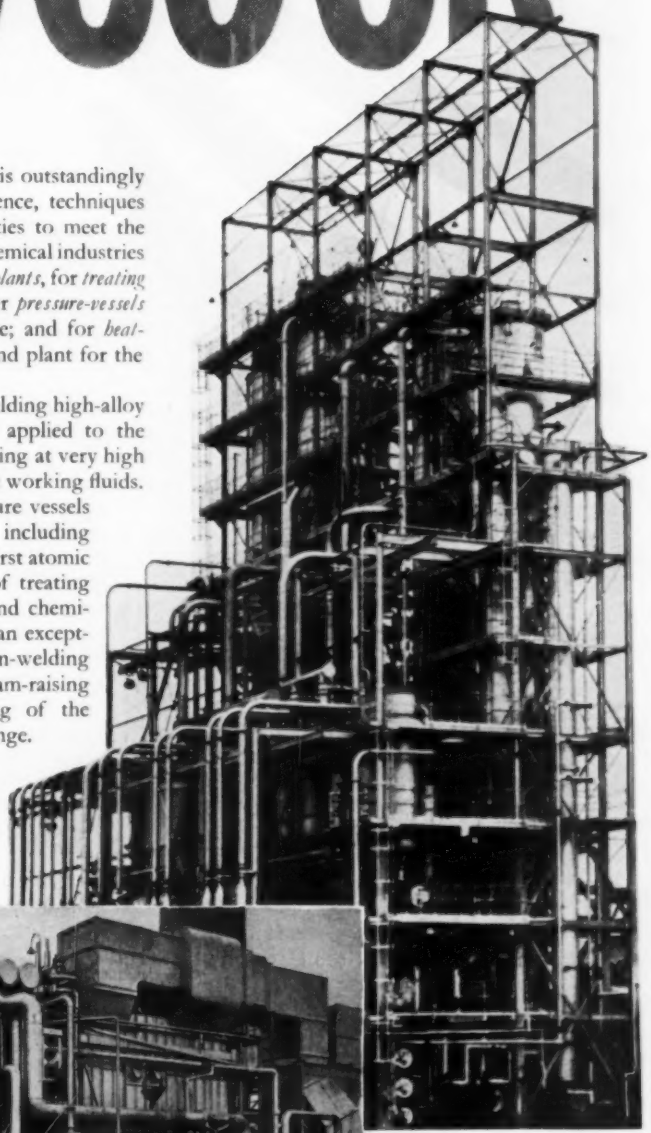


Heat-exchanger built by Babcock for service in an oil refinery.



One of a number of Babcock Integral-Furnace boilers, fired by refinery-gas and- or oil; in an "outdoor" type installation, at a large oil refinery.



Distillation unit at an oil refinery comprising Babcock fusion-welded columns.

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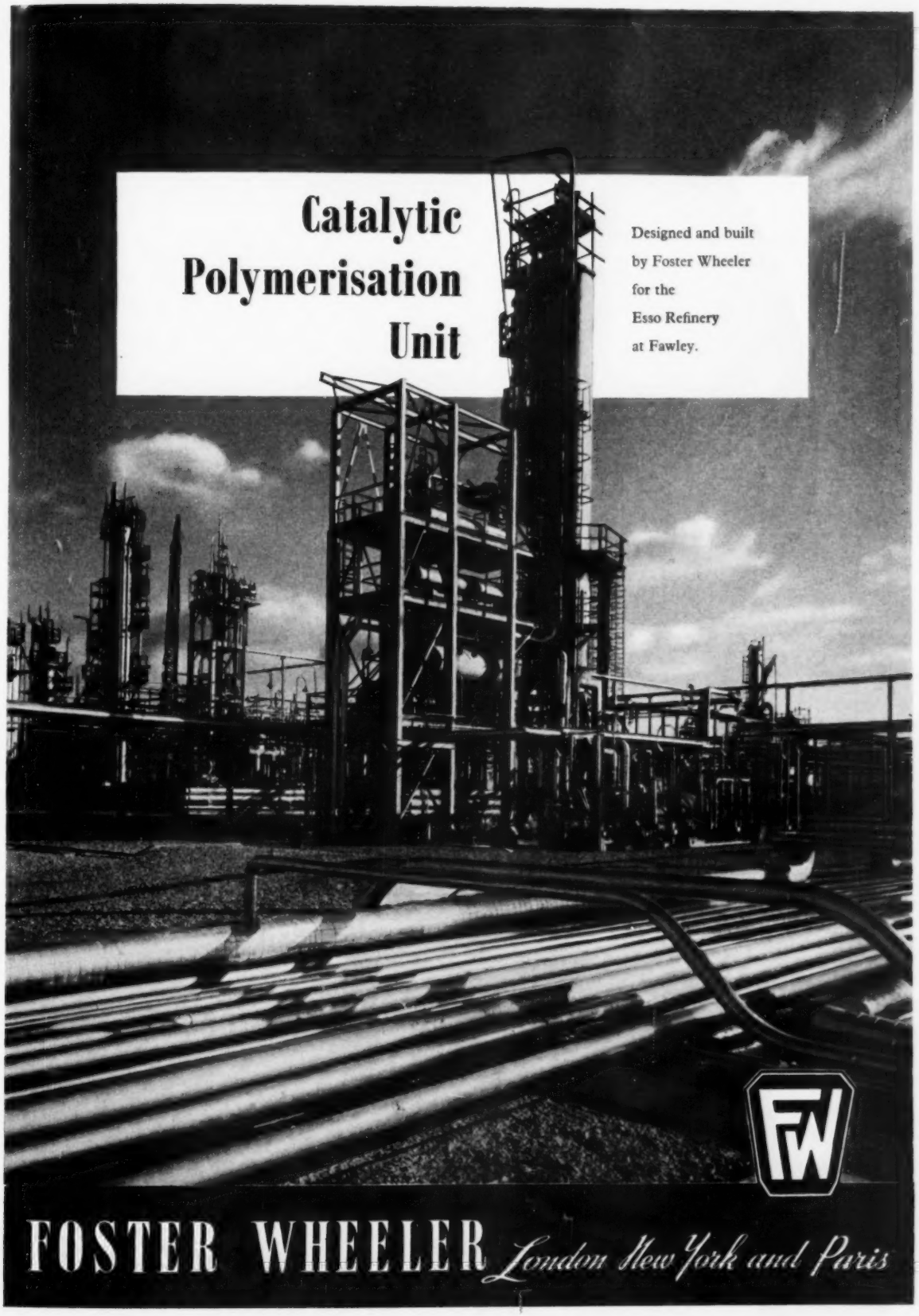
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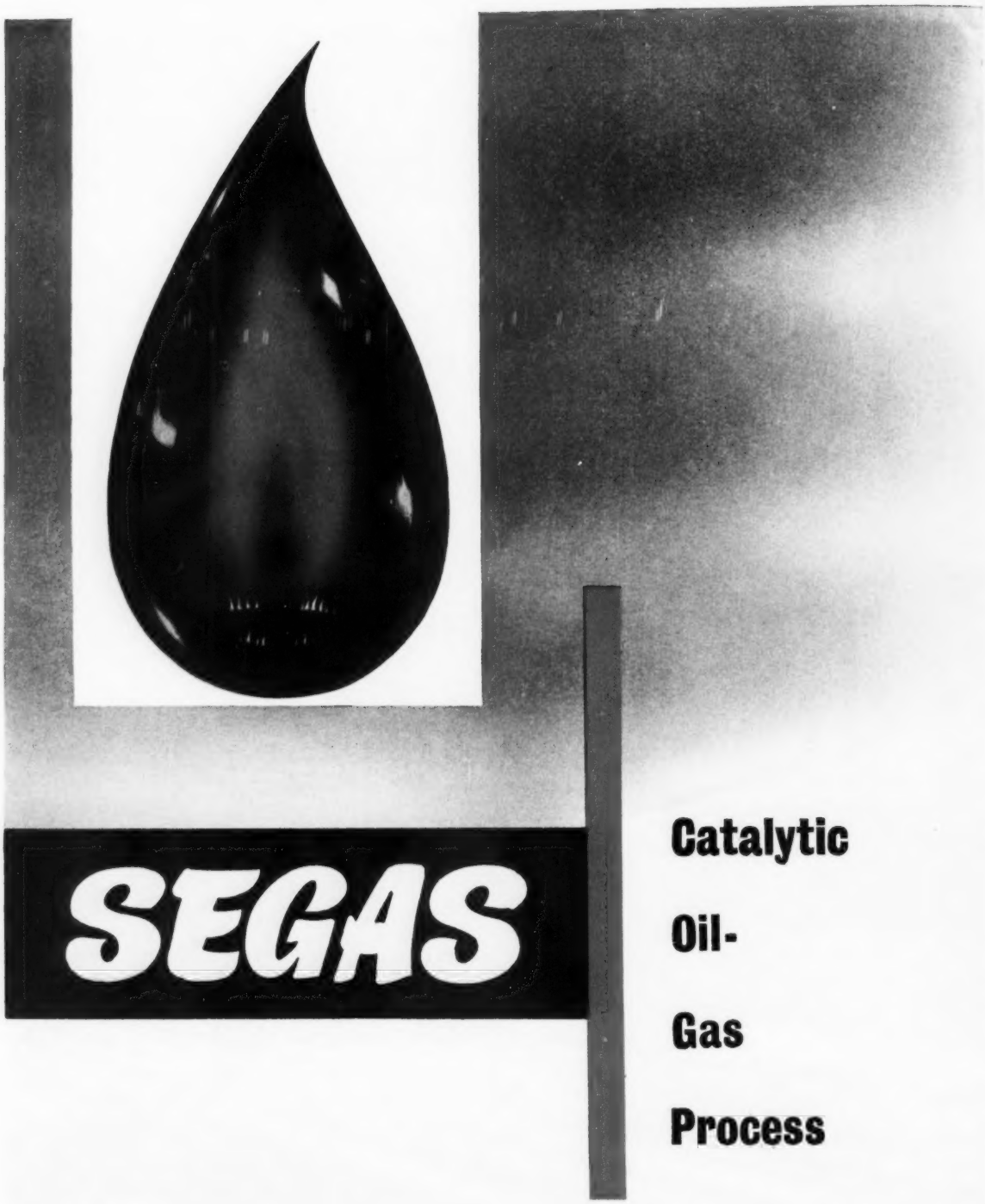

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